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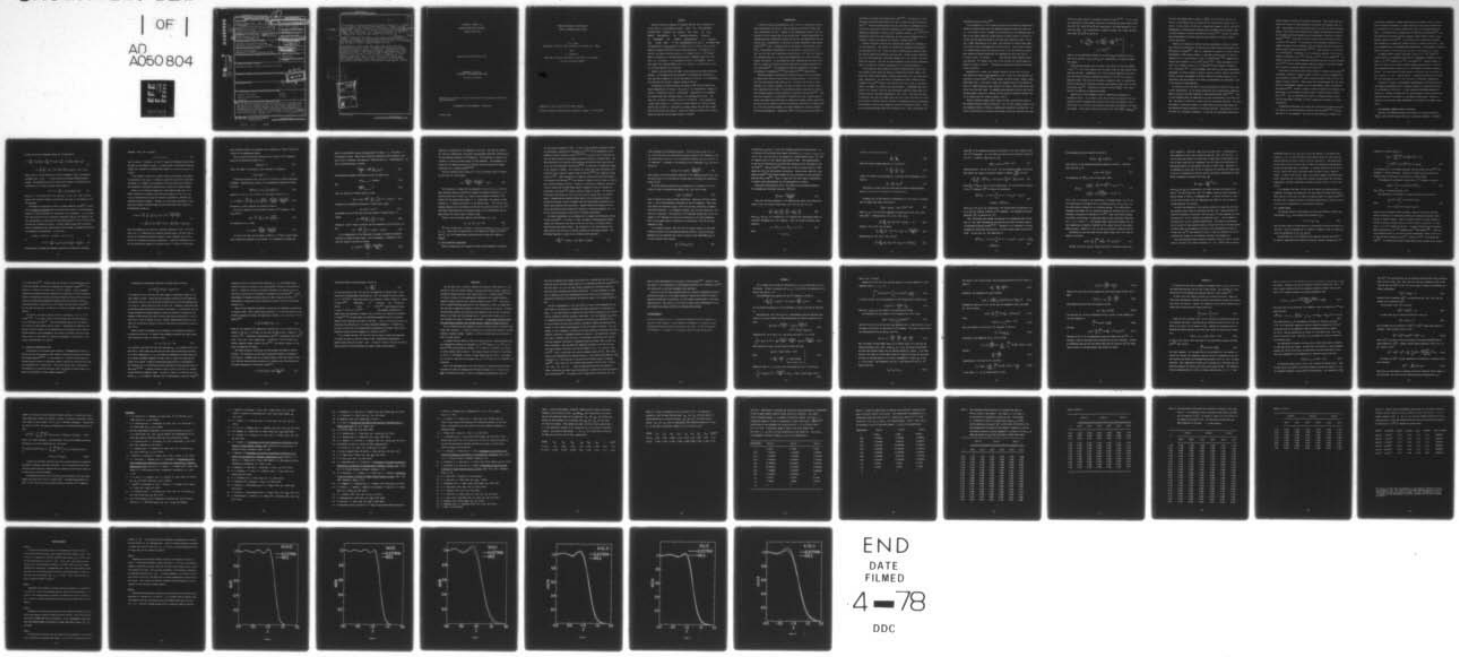

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Charge on electron-hole drop (EHD) is also studied in the above mentioned systems. In accordance with the experiment of Pokrovsky and Svistunova, we find that EHD is negative in Ge(4;2) and positive in Ge(1;2). It is predicted that the drop will sustain a negative charge in Ge(1;1).

Calculations for surface tension and charge on EHD are also reported in three configurations of silicon. The value of σ in unstressed Si, denoted by Si(6;2), is obtained to be 87.4 x 10^{-4}erg/cm^2. Application of an intermediate stress along <100> direction leads to the configuration Si(2;2). The value of σ in Si(2;2) is found to be 32.8 x 10^{-4}erg/cm^2. In the presence of a large <100> stress, i.e., in Si(2;1), surface tension is a factor of eight smaller than in Si(6;2). Calculation of charge reveals that the EHD is negative in both Si(6;2) and Si(2;1). Within the limits of accuracy of our calculation we find the drop is almost neutral in Si(2;2).

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January 1978

SURFACE STRUCTURE OF ELECTRON-HOLE DROPS IN GERMANIUM AND SILICON*

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ABSTRACT

Density functional formalism of Hohenberg and Kohn (HK) is generalized for the case of a multicomponent plasma. Using the self-consistent Kohn-Sham (KS) equations for electrons and holes and local density approximation for exchange-correlation potential, we investigate the surface characteristics of electron-hole liquid (EHL) in six configurations of Ge and Si. We denote these configurations by $X(\nu_e;\nu_h)$, where X is either Ge or Si, and ν_e and ν_h are the number of occupied electron and hole bands, respectively. In normal Ge, i.e., Ge(4;2), the value of surface tension, σ, is found to be 3.7×10^{-4} erg/cm^2. When Ge is subject to a uniform stress of about 3.5kg/mm^2 along <111> direction, i.e., in Ge(1;2), σ is calculated to be 1.0×10^{-4} erg/cm^2. Under a very large <111> uniaxial stress on Ge, i.e., Ge(1;1), σ is found to be a factor of twenty smaller than in Ge(4;2).

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Calculations for surface tension and charge on EHD are also reported in three configurations of silicon. The value of σ in unstressed Si, denoted by Si(6;2), is obtained to be 87.4×10^{-4} erg/cm^2. Application of an intermediate stress along <100> direction leads to the configuration Si(2;2). The value of σ in Si(2;2) is found to be 32.8×10^{-4} erg/cm^2. In the presence of a large <100> stress, i.e., in Si(2;1), surface tension is a factor of eight smaller than in Si(6;2). Calculation of charge reveals that the EHD is negative in both Si(6;2) and Si(2;1). Within the limits of accuracy of our calculation we find the drop is almost neutral in Si(2;2).

INTRODUCTION

In indirect band gap semiconductors (e.g., Ge or Si) excitons are formed under weak external excitation. When the density of excitons becomes high, their individuality is lost. Further, in the luminescence spectra a new line appears on the low energy side of the exciton line. Detailed experimental investigations have consistently pointed out that the new luminescence line originates from a recombination of electrons and holes condensed in high density droplets[1-16]. Such a condensed state is now known as electron-hole liquid (EHL). Experimental investigation of its properties is facilitated by the fact that the life time of particles is quite long (~ 10^{-6} sec) and therefore the condensed phase is, to a very good approximation, in a state of thermodynamic equilibrium. It was Keldysh who first conceived that the EHL is likened to a plasma of electrons and holes stabilized by Coulomb interaction of the constituents[17]. His conception of EHL was subsequently confirmed by an abundance of experimental[1-16] and theoretical[18-26] observations.

Theoretical appeal in electron-hole liquid is mainly due to the absence of complications which can arise from the lattice effects. In view of the fact that the excitonic Bohr radius in Ge (~ 177 Å) or Si(~ 49 Å) is large compared to the lattice constant, and that the fraction of electrons excited into conduction band is small, the interaction between electrons and holes is bare Coulomb screened by static dielectric constant of the material[27]. Thus, EHL can be regarded as a collection of electrons and holes, characterized by proper band masses and interacting via statically screened Coulomb interaction. The fact that the system at hand can be accurately described as a quantum plasma of electrons and holes makes it an ideal candidate for testing different many-body approximations. Theoretical efforts to date have been successful in

explaining the ground state properties of EHL[20-26]. Calculations of binding energy and equilibrium density in Ge and Si agree very well with experiment[26]. Detailed investigations have also been made of thermodynamic quantities like, gas-liquid transition temperature, the compressibility, the temperature dependence of density and of chemical potential, etc.[16,26,28-33]. Theoretical results for these quantities are also in good agreement with experiments, thereby establishing the validity of plasma model[26].

Surface structure of EHL has not hitherto been examined as thoroughly as its bulk properties. The reasons for insufficient knowledge of EHL surface are essentially two fold. First, the lack of translational invariance makes any surface problem more difficult than the bulk. Second, proper understanding of the bulk properties, which must precede that of the surface, has come about only recently. Now that the bulk properties of EHL are well understood, there is a basis for a proper investigation of its surface properties.

In this paper we shall examine the surface characteristics, such as surface tension, dipole layer and charge on electron-hole droplet (EHD) in germanium and silicon under uniform, uniaxial stress along <111> and <100> directions, respectively. For the sake of convenience we shall designate these systems by $X(\nu_e;\nu_h)$[34] where X is either Ge or Si, and ν_e and ν_h are, respectively, the number of conduction and valence bands. In germanium under zero stress, i.e., Ge(4;2), there are four equivalent conduction bands along <111> direction and two hole bands degenerate at the Γ point. Away from the center of Brillouin zone, the hole bands branch out into a light and heavy hole bands. The structure of valence bands is the same in unstrained silicon and germanium. The difference arises in the number and location of conduction valleys. There are six conduction bands along <100> direction in Si. Thus, the notation for

unstrained silicon is Si(6;2)[35].

In the presence of a <111> stress on Ge, one of the conduction minima moves toward the valence bands while the remaining conduction bands move away from it. At a stress of about 3.5kg/mm^2 all the electrons of the condensed phase reside in the lowest conduction valley, because the Fermi energy of electrons coincides with the absolute minima of the other three conduction bands. Except for a slight decoupling at the Γ point, the structure of valence bands remain as in Ge(4;2). Such a configuration is called Ge(1;2). When silicon is subject to a uniform stress along <100> direction, two of the six conduction valleys move toward the valence bands while the remaining four move away from it. At a stress of about 10.5 kg/mm^2, only the two lowest conduction bands are populated. The changes that occur in the structure of valence bands are similar to those in Ge(1;2). Following our notation we denote this configuration by Si(2;2).

Application of a large <111> uniaxial stress in Ge and <100> in Si not only removes the valence band degeneracy at the Γ point, but also modifies the structure of valence bands.[36] In both systems, the holes occupy a single, highly anisotropic band. In Ge under a large <111> uniaxial stress the electrons reside in a single conduction band, whereas in Si under a large <100> stress they occupy two conduction bands. We designate these systems by Ge(1;1) and Si(2;1). The band masses, dielectric constant, and the values of excitonic rydberg used in the present work are listed in Tables I and II.

Owing to different masses and/or number of bands, electrons and holes in EHL possess different chemical potentials. Now, the bulk chemical potential for any component consists of kinetic, exchange and correlation contributions. Explicit calculations for the ground state energy reveal that electrons and holes

contribute almost equally to exchange-correlation energy[21-26]. In that event, the difference in bulk chemical potentials of electrons and holes arises mainly from $(\bar{\mu}_e^T - \bar{\mu}_h^T)$, where $\bar{\mu}_e^T$ and $\bar{\mu}_h^T$ are, respectively, the Fermi energies of electrons and holes. For a system with ν_e conduction bands, and a light and heavy hole bands, $\bar{\mu}_e^T$ and $\bar{\mu}_h^T$ are given by

$$\left.\begin{aligned} \bar{\mu}_e^T &= \frac{\hbar^2 K_o^2}{2m_{de}\nu_e^{2/3}} \; ; \; \bar{\mu}_h^T = \frac{\hbar^2 K_o^2}{2m_{hh}}\left[1 + \left(\frac{m_{\ell h}}{m_{hh}}\right)^{3/2}\right]^{-2/3} \\ \text{and} \quad K_o &= (3\pi^2 n_o)^{1/3} \end{aligned}\right\} \tag{1}$$

where n_o is the equilibrium density of e-h pairs, m_{de} the density of states mass for an electron, and $m_{\ell h}$ and m_{hh} are, respectively, the light and heavy hole masses.

Using the band masses, given in Table I, for Ge(4;2) we find that $\bar{\mu}_e^T/\bar{\mu}_h^T = 1.62/\nu_e^{2/3} = 0.64$, which implies that the holes in EHL are less tightly bound than the electrons. Consequently, at a low but finite temperature the holes will have excess thermionic emission and, therefore, the EHD will sustain a negative charge. The holes will continue to evaporate until, at equilibrium, the work functions for electrons and holes, and therefore their rates of emission become equal[37]. Similarly, in Si(6;2) the ratio $\bar{\mu}_e^T/\bar{\mu}_h^T = 0.55$, implying that the EHD will be negatively charged.

Application of these arguments leads to interesting consequences in strained Ge and Si. It is easy to infer that in Ge(1;2) and Si(2;2) the electrons will tend to evaporate more than the holes (the ratio $\bar{\mu}_e^T/\bar{\mu}_h^T = 1.62$ in Ge(1;2) and 1.14 in Si(2;2)) and therefore the droplet will acquire a net positive charge. In the case of Ge(1;1) and Si(2;1) the ratio $\bar{\mu}_e^T/\bar{\mu}_h^T = m_{dh}/m_{de}\nu_e^{2/3}$.

With the band masses given in Table II, $\bar{\mu}_e^T/\bar{\mu}_h^T$ = 0.40 in Ge(1;1) and 0.46 in Si(2;1), which implies that the electrons will evaporate less readily than the holes. In other words, the EHD will be negatively charged in Ge(1;1) and Si(2;1). Measurements of Pokrovsky and Svistunova have confirmed that the charge on EHD is indeed negative in Ge(4;2) and positive in Ge(1;2)[38]. To date, no experimental measurement of droplet charge has been reported in Ge(1;1), Si(6;2), Si(2;2) and Si(2;1).

Coming to the question of surface tension, experimental studies of coexistence curve have revealed that the exciton gas becomes supersaturated before the EHD begins to nucleate[39]. This is a signature of existence of surface tension. Measurements of EHL surface tension, σ, have been carried out only in Ge(4;2). Westervelt et al. have reported a value of $2.9*10^{-4}$ erg/cm^2 [39]. Bagaev and coworkers have estimated σ to be $1.6*10^{-4}$ erg/cm^2 [40]. Recent experiment of Etienne et al. reveals a value of $3 * 10^{-4}$ erg/cm^2 [41] while Staehli's estimate is $3.8 * 10^{-4}$ erg/cm^2 [42]. To our knowledge, there does not exist any experimental measurement of surface tension in Ge(1;2), Ge(1;1), Si(6;2), Si(2;2), and Si(2;1). Without conclusive experiments on surface tension and binding energy it is inconceivable that any progress can be made in understanding the coexistence curve or the kinetics of EHD formation.

In view of the fact that EHL is free from "parasitic" effects of ions, theoretical investigation of its surface properties can be appropriately handled by means of density functional formalism of Hohenberg-Kohn-Sham (HKS)[43-45]. Within this formalism there are essentially two ways of approaching the surface problem. The easier of these two is widely known as variational procedure. The basic philosophy of variational method is to approximate the ground state energy and use exponential density profiles for electrons and holes. Each density is characterized by a variational parameter. In this way the approximate ground state

energy becomes a function of variational parameters. After minimizing total energy with respect to these parameters one obtains the minimized total energy. Subtracting the bulk contribution from the total, one gets the surface energy. Most authors have retained local density contributions from kinetic and exchange-correlation energies, and first gradient correction to kinetic energy[37,46-49]. The value of surface tension that they obtain in Ge(4;2) is around $1*10^{-4}$ erg/cm^2. On including the first gradient correction to exchange-correlation energy Vashishta, Kalia and Singwi find that the value of surface tension changes significantly[50,51]. Their estimate of σ in Ge(4;2) is $3.5*10^{-4}$ erg/cm^2. Evidently, it is in reasonable agreement with the measurement of Westervelt et al.[39], Etienne et al.[41], and of Staehli[42]. An important outcome of their variational calculation as well as that of Reinecke et al.'s[49] is that the EHD surface tension in Ge(4;2) is an order of magnitude (a factor of sixteen) larger than in Ge(1;1).[50]

Variational calculations that include effects of valence band coupling[48] on gradient correction to kinetic energy of holes, as well as exchange-correlation gradient correction[50], yield a positive charge on EHD in Ge(4;2) and negative charge in Ge(1;2). These results are in disagreement with the above mentioned thermodynamic arguments and the experimental results of Pokrovsky and Svistunova[38]. Further, contrary to what one expects from energetic considerations, the variational procedure yields a positive charge on EHD in Ge(1;1)[50]. Such an unsatisfactory feature of variational method arises from the approximate treatment of kinetic energy and the absence of Friedel oscillations.

Considerable improvement can be made over variational procedures, provided one resorts to the self-consistent scheme of Kohn and Sham[44,45]; the work involved in it is stupendous. The merit of self-consistent procedure lies

in the exact treatment of kinetic energy which also brings in part of the effect of Friedel oscillations. We shall describe in this paper a self-consistent calculation for the surface properties of EHL in the aforementioned systems. In accordance with the observation of Pokrovsky and Svistunova[38], the self-consistent calculation yields a negative charge on EHD in Ge(4;2), and a positive charge in Ge(1;2)[52]. On the basis of our calculation we predict that the EHD will be negatively charged in Ge(1;1), Si(6;2), and Si(2;1). This is in agreement with the aforementioned thermodynamic considerations. Within the limit of accuracy of the calculation, the EHD is found neutral in Si(2;2).

As regards surface tension, we obtain a value of $3.7 * 10^{-4}$ erg/cm^2 in Ge(4;2) which is in reasonable accord with the experimental estimates of Westervelt et al.[39], Etienne et al.[41], and Staehli[42]. Surface tension in Ge(1;1) is found to be a factor of twenty smaller than in Ge(4;2). The present calculation yields a value of $87.4 * 10^{-4}$ erg/cm^2 for surface tension in Si(6;2). As in the case of Ge under stress, we find that the σ in Si(2;1) is much smaller ($\simeq 1/8$) than in Si(6;2). In Ge(1;2) and Si(2;2) the values of σ are calculated to be $1.0 * 10^{-4}$ and $32.8 * 10^{-4}$ erg/cm^2, respectively.

In Section I we give a multicomponent generalization of HK theory and derive rigorous expressions for the chemical potential of electrons and holes. It is followed by a description of self-consistent Kohn-Sham equations in Section II. Section III deals with the surface tension of EHD in the six systems and Section IV is devoted to a discussion of EHD charge. Finally, we mention in the conclusion what improvements can be made on the present calculation.

I. MULTICOMPONENT GENERALIZATION OF HK THEORY

Consider an M-component system in the presence of external potentials $\{V_e^i(\underline{r})\}$, each of which couples with only a particular component. The Hamil-

tonian of such an M component system can be expressed as

$$H = \sum_{i=1}^{M} \int d\underline{r}\, \Psi_i^+(\underline{r})\, (-\frac{\hbar^2}{2m_i} \nabla^2)\, \Psi_i(\underline{r}) + \sum_{i=1}^{M} \int d\underline{r}\, \Psi_i^+(\underline{r})\, V_e^i(\underline{r})\, \Psi_i(\underline{r}) \tag{2}$$

$$+ \ 1/2 \sum_{i=1}^{M} \sum_{j=1}^{M} \int d\underline{r} \int d\underline{r}'\, \Psi_i^+(\underline{r})\, \Psi_j^+(\underline{r}') v_{ij}(\underline{r}-\underline{r}')\, \Psi_j(\underline{r}')\, \Psi_i(\underline{r}),$$

where $\Psi_i(\underline{r})$ is a field operator for the i^{th} component, $\Psi_i^+(\underline{r})$ its Hermitian conjugate, and $v_{ij}(\underline{r})$ is the statically screened Coulomb potential energy. The expectation value of H taken with respect to the ground state wavefunction $|\Psi>$ yields the ground state energy, E:

$$E = T + V + \sum_{i=1}^{M} e\, \xi_i \int d\underline{r}\, V_e^i(\underline{r})\, n_i(\underline{r}) \ , \tag{3}$$

where $\xi_i = +1$ for holes and -1 for electrons. In Eq. (3), T and V are the kinetic and potential energies, respectively, and $n_i(\underline{r})$ is the density of the i^{th} component.

Following the proof given by HK for a single component system,[43] we shall show by reductio ad absurdum that the ground state energy of a multicomponent system is a unique functional of the density of each component. Let us assume that there exists two sets of external potentials, $\{V_{e\alpha}^i(\underline{r})\}$ and $\{V_{e\beta}^i(\underline{r})\}$, and that corresponding to them there are two wavefunctions $|\Psi>$ and $|\Psi'>$ which yield the same set of densities $\{n_i(\underline{r})\}$. We shall further assume that the ground state is nondegenerate and that the ground state energy is minimum with respect to variations in wavefunction. In that case,

$$(\psi|H|\psi) < (\psi'|H|\psi') = (\psi'|H'|\psi') + (\psi'|H - H'|\psi') \tag{4}$$

or

$$E < E' + \sum_{i=1}^{M} e\, \xi_i \int d\underline{r}\, n_i(\underline{r})\, [V_{e\alpha}^i(\underline{r}) - V_{e\beta}^i(\underline{r})] \tag{5}$$

Interchanging the primed and unprimed quantities and adding the resulting

equation to Eq. (5), we obtain

$$E + E' < E + E' \ , \tag{6}$$

which is absurd. Therefore, $|\Psi\rangle$ and $|\Psi'\rangle$ cannot be different and yet yield the same set of densities $\{n_i(\underline{r})\}$. In other words, the external potentials $\{V_e^i(\underline{r})\}$ and, therefore, the ground state energy are uniquely determined by $\{n_i(\underline{r})\}$.

If the number of particles is fixed, E must be stationary with respect to variations in any $n_i(\underline{r})$. A change in $n_i(\underline{r})$ from its correct value shall correspond to a change in the wavefunction from the ground state function and according to variational principle such a state is of higher energy.

Insofar as the potential energy has a long range Coulomb part, it is hardly convenient to express the ground state energy as in Eq. (3), i.e., a sum of contributions arising from external perturbation, potential and interacting kinetic energies. Instead, it is much more appropriate to separate the classical Coulomb energy and write the ground state energy of a multicomponent plasma as

$$E[\{n_i\}] = \frac{e^2}{2\kappa} \sum_{i=1}^{M} \sum_{j=1}^{M} \xi_i \xi_j \int d\underline{r}' \int d\underline{r}'' \ \frac{n_i(\underline{r}')n_j(\underline{r}'')}{|\underline{r}' - \underline{r}''|} \tag{7}$$

$$+ e \sum_{i=1}^{M} \xi_i \int d\underline{r}' \ V_e^i(\underline{r}') \ n_i(\underline{r}') + \sum_{i=1}^{M} T_s^i[n_i] + E_{xc}[\{n_i\}] \ ,$$

where the summations are taken over different components of EHL. The first term in Eq. (7) constitutes the classical Coulomb energy, the third term is the sum of noninteracting kinetic energies of each component and the last term is the exchange-correlation contribution. A distinct advantage of writing the ground state energy in a form such as Eq. (7) lies in the ease with

which different terms in the equation can be expressed in terms of quantities related to the homogeneous system.

Let δn_ℓ denote an arbitrary variation in the density of ℓ^{th} component. Owing to the stationary property of E,

$$\delta_\ell E[\{n_i\}] = 0 \quad . \tag{8}$$

Since, the number of particles of each component is conserved,

$$\int d\underline{r}\ \delta n_\ell(\underline{r}) = 0 \tag{9}$$

Conditions expressed in Eqs. (8) and (9) are basic to density functional formalism. Combining them by means of an undetermined Lagrange multiplier, we obtain

$$\delta\left(E[\{n_i\}] - \sum_\ell \mu_\ell \int d\underline{r}\ n_\ell(\underline{r})\right) = 0 \tag{10}$$

Using Eq. (7) in Eq. (10) we obtain the following expression for μ_ℓ:

$$\mu_\ell = e\,\xi_\ell V_e^\ell(r) + \frac{e^2\xi_\ell}{\kappa} \sum_{j=1}^{M} \xi_j \int d\underline{r}' \frac{n_j(\underline{r}')}{|\underline{r} - \underline{r}'|} + \frac{\delta T_s^\ell[n_\ell]}{\delta n_\ell(\underline{r})} + \frac{\delta E_{xc}[\{n_i\}]}{\delta n_\ell(\underline{r})} \tag{11}$$

Henceforth, we shall suppress the external potential.

Let $\xi_\ell\phi(r)$ represent the electrostatic energy of ℓ^{th} component. With $\phi(\underline{r})$ given by

$$\phi(\underline{r}) = \frac{e^2}{\kappa} \sum_{j=1}^{M} \xi_j \int d\underline{r}' \frac{n_j(\underline{r}')}{|\underline{r} - \underline{r}'|}\ , \tag{12}$$

the expression for μ_ℓ reads,

$$\mu_\ell = \xi_\ell\phi(\underline{r}) + \frac{\delta T_s^\ell[n_\ell]}{\delta n_\ell(\underline{r})} + \frac{\delta E_{xc}[\{n_i\}]}{\delta n_\ell(\underline{r})} \quad . \tag{13}$$

In view of the fact that the radius of EHD ($\gtrsim 5 \times 10^{-4}$cm) is much larger than interparticle distance in the system, it is reasonable to assume that

EHL is a semi-infinite system, occupying half the space $z < 0$. The space $z > 0$ is treated as vacuum. Under these conditions, densities of EHL components vary only in the z direction, thus making ϕ a function only of z. Transforming Eq. (12) into a Poisson equation, we obtain

$$\frac{d^2\phi(z)}{dz^2} = -\frac{4\pi e^2}{\kappa} \sum_{j=1}^{M} \xi_j \, n_j(z) \quad . \tag{14}$$

The appropriate boundary conditions for $\phi(z)$ are taken to be,

$$\phi(z)\Big|_{z \to +\infty} = \text{constant} \tag{15a}$$

and

$$\frac{d\phi(z)}{dz}\Big|_{z \to +\infty} = 0 \tag{15b}$$

Then, the solution of Poisson equation reads,

$$\phi(z) = \phi(\infty) + \frac{4\pi e^2}{\kappa} \sum_{j=1}^{M} \xi_j \int_z^{\infty} dz' \, (z - z') n_j(z') \tag{16}$$

Following the conventional definition of dipole layer, namely

$$\Delta\phi = \phi(\infty) - \phi(-\infty) \, , \tag{17}$$

and making use of the fact that the total system is charge neutral, we obtain

$$\Delta\phi = \frac{4\pi e^2}{\kappa} \sum_{j=1}^{M} \xi_j \int_{-\infty}^{\infty} dz' \, z' \, n_j(z) \tag{18}$$

Writing Eq. (18) in terms of electron and hole densities, $n_e(z)$ and $n_h(z)$, we get

$$\Delta\phi = -\frac{4\pi e^2}{\kappa} \int_{-\infty}^{\infty} dz' \, z' \, [n_e(z') - n_h(z')] \tag{19}$$

It is consequential to the discussion of charge to express the chemical potential in terms of dipole layer. For this purpose, we average Eq. (13) over the volume of the drop and obtain

$$\mu_\ell = \xi_\ell \phi(-\infty) + \frac{\delta T_s^\ell[\bar{n}_\ell]}{\delta \bar{n}_\ell} + \frac{\delta E_{xc}[\{\bar{n}_i\}]}{\delta \bar{n}_\ell} \, , \tag{20}$$

where $\bar{n}_\ell$ is the density of ℓ^{th} component in the bulk. The last two terms in Eq. (20) are, respectively, the kinetic and exchange-correlation contributions to bulk chemical potential of ℓ^{th} component. The expression for kinetic contribution is simply the Fermi energy for that component. The exchange-correlation part of chemical potential is obtained from the ground state energy calculation for a uniform system[23,26].

From now onwards we shall take $\phi(\infty) = 0$ as our reference level of energy. In that case, Eq. (20) becomes

$$\mu_\ell = \frac{\delta T_s^\ell[\bar{n}_\ell]}{\delta \bar{n}_\ell} + \frac{\delta E_{xc}[\{\bar{n}_i\}]}{\delta \bar{n}_\ell} - \xi_\ell \Delta\phi \ , \qquad (21)$$

The discussion of charge that we presented in the introduction can now be made completely general provided one compares the chemical potential, μ_e, of electrons with that of holes, μ_h. Since the bulk chemical potential is obtained from the ground state energy of a uniform EHL, the quantity of main interest in a surface calculation is the dipole layer. The dipole layer depends sensitively on the density profiles for electrons and holes, [Eq. (19)] and unless these densities are accurately known, it is inconceivable that we shall obtain the correct sign of charge on EHD,

From Eq. (21) we can write down for the difference $(\mu_h - \mu_e)$;

$$\mu_h - \mu_e = \bar{\mu}_h - \bar{\mu}_e - 2\Delta\phi \qquad (22)$$

The sign and magnitude of charge is completely determined by the difference $\mu_h - \mu_e$. Since twice the dipole layer is not expected to remove the difference $\bar{\mu}_h - \bar{\mu}_e$, the aforementioned conclusions about charge will remain unchanged.

II. SELF-CONSISTENT CALCULATION

There are essentially two reasons for doing a self-consistent calculation

for the surface properties of EHL. In view of the reasonable agreement between the variational calculation of Vashishta et al.[50] and the experimental measurement of surface tension in Ge(4;2)[39,41,42], one would like to know what effect the higher kinetic and exchange-correlation gradient corrections have. The other motivation for doing the self-consistent calculation stems from the failure of all the variational calculations[48-50] in providing a satisfactory answer to the question of charge. Let us remind our reader that these variational calculations yield a positive charge on EHD in Ge(4;2)[48,50] and a negative charge in Ge(1;2)[50]. These features are in complete contradiction with the findings of Pokrovsky and Svistunova[38]; they measure a negative droplet charge in Ge(4;2) and a positive charge in Ge(1;2). Further, on the basis of energetic considerations we showed that the EHD charge would be negative in Ge(1;1), whereas the variational calculation[50] yields a positive charge on the EHD. The failure of variational calculations is due to the fact that the dipole layer is overestimated. Considering how sensitive dipole layer is to the density profiles of electrons and holes, the way to improve upon the variational calculations is to obtain these densities more accurately. Another serious shortcoming in variational calculations arises because of truncation of gradient expansion, as a result of which one misses out the effect of Friedel oscillations.

All these shortcomings can be remedied by the elegant self-consistent scheme of Kohn and Sham[44]. It allows an exact treatment of noninteracting kinetic energy, and consequently one does not miss out the effect of Friedel oscillations arising from kinetic energy. The limitation of the self-consistent procedure lies in how well one can include exchange and correlation effects. The Kohn-Sham formalism is based on the following three equations:

$$\left(-\frac{\hbar^2}{2m_\ell}\nabla^2 + V_\ell[\{n_i\}\,;\,\underline{r}]\right)\psi_\ell^\alpha(\underline{r}) = \varepsilon_\ell^\alpha\,\psi_\ell^\alpha(\underline{r}) \qquad (23)$$

which resembles the Schrödinger equation. The first term on the l.h.s. of Eq. (23) arises from the noninteracting kinetic energy of ℓ^{th} component of EHL. The second term on the l.h.s. is the effective potential felt by a particle of ℓ^{th} component. It depends on the densities of all components, $\{n_i\}$, and can be written as

$$V_\ell[\{n_i\}: \underline{r}] = \xi_\ell \phi(\underline{r}) + \frac{\delta E_{xc}[\{n_i\}]}{\delta n_\ell(\underline{r})} \quad , \tag{24}$$

where $\xi_\ell \phi(\underline{r})$ is the electrostatic potential of ℓ^{th} component, given by Eq. (12), and $\delta E_{xc}/\delta n_\ell(\underline{r})$ is the contribution arising from the exchange and correlation energy of EHL.

The third equation constitutes an expression for the density of ℓ^{th} component in terms of eigensolutions, $\psi_\ell^\alpha(\underline{r})$, of Eq. (23), and it reads

$$n_\ell(\underline{r}) = \sum_\alpha |\psi_\ell^\alpha(\underline{r})|^2 \tag{25}$$

where α denotes the lowest occupied eigenstates. Equations (23)-(25) constitute a set of self-consistent equations for the ℓ^{th} component. Their solution yields the densities $\{n_i(\underline{r})\}$, which are the basic quantities in density functional formalism. It is apparent from Eqs. (23)-(25) that these are a coupled set of equations - the potential of ℓ^{th} component depends not only on the density of ℓ^{th} component but also on the densities of all other components. This is the primary source of difficulty in solving Eqs. (23)-(25) for each component of EHL.

It is evident from Eqs. (23)-(25) that the central quantity in the self-consistent method is the exchange-correlation potential, $\delta E_{xc}[\{n_i\}]/\delta n_\ell(\underline{r})$. Assuming that the densities vary slowly in space, we may approximate E_{xc} by the local density term, whereby

$$E_{xc} \simeq \int d\underline{r}\, \epsilon_{xc}(\{n_i\}) \tag{26}$$

The quantity, $\epsilon_{xc}(\{n_i\})$, is the total exchange-correlation energy density. It is obtained from the ground state energy calculation for a system of uniform densities $\{\bar{n}_i\}$, and then each $\bar{n}_i$ is replaced by a varying density $n_i(\underline{r})$. Eq. (26) is commonly known as local density approximation (LDA). The appropriateness of LDA for the determination of ground state energy was first discussed by Kohn and Sham[44]. Tong and Sham[53] showed that in LDA the density $n(\underline{r})$ for atoms agrees well with the Hartree-Fock calculations. Using an exact sum rule, Vanni-menus and Budd[54] have argued strongly for the correctness of $n(\underline{r})$ obtained by Lang and Kohn in LDA[55]. Thus, it seems that the local density approximation is indeed a good approximation for the determination of density.

Functional differentiation of Eq. (26) leads to the following expression for exchange and correlation potential, $\mu_\ell^{xc}(\{n_i\})$:

$$\mu_\ell^{xc}(\{n_i\}) = \frac{\partial \epsilon_{xc}(\{n_i\})}{\partial n_\ell(\underline{r})} \quad . \tag{27}$$

Since the particles belonging to ℓ^{th} component may reside in an anisotropic elliptic band, the kinetic energy term in Eq. (23) may have the form

$$\frac{\nabla^2}{2m_\ell} \equiv \frac{1}{2m_{\ell,t}} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right) + \frac{1}{2m_{\ell,\ell}} \frac{\partial^2}{\partial z^2} \, , \tag{28}$$

where $m_{\ell,t}$ and $m_{\ell,\ell}$ are, respectively, the tranverse and longitudinal masses of a particle belonging to the ℓ^{th} component. Under the volume conserving transformation

$$x = \gamma^{-\frac{1}{6}} \underset{\sim}{x} \; ; \; y = \gamma^{-\frac{1}{6}} \underset{\sim}{y} \; ; \; z = \gamma^{\frac{1}{3}} \underset{\sim}{z} \tag{29}$$

where

$$\gamma = m_{\ell,t}/m_{\ell,\ell}$$

Equation (28) takes up the form

$$\frac{\nabla^2}{2m_\ell} = \frac{\underset{\sim}{\nabla}^2}{2\bar{m}_\ell} \tag{30}$$

where the kinetic energy operator, $\underset{\sim}{\nabla}^2$, is given by

$$\underset{\sim}{\nabla}^2 \equiv \frac{\partial^2}{\partial \underset{\sim}{x}^2} + \frac{\partial^2}{\partial \underset{\sim}{y}^2} + \frac{\partial}{\partial \underset{\sim}{z}^2} , \tag{31}$$

and $\bar{m}_\ell$, the density of states mass for a particle of ℓ^{th} component, is defined by

$$\bar{m}_\ell = (m_{\ell,t}^2 \; m_{\ell,\ell})^{\frac{1}{3}} \tag{32}$$

Henceforth, we shall drop the tilde from the kinetic energy operator, and omit the bar over the density of states mass, $\bar{m}_\ell$.

Assuming that the EHL surface is perpendicular to the z-axis, the expression for $\psi_\ell^\alpha(\underline{r})$ deep inside the liquid is

$$\psi_\ell^\alpha(\underline{r}) \propto \sin(kz - \gamma(k)) \; e^{i(k_x x + k_y y)} \tag{33}$$

where k_x, k_y, k are the three components of wave vector $\underline{k}$ and $\gamma(k)$ is the phase shift. Substituting Eq. (33) in Eq. (23), we get

$$\varepsilon_\ell^\alpha = \frac{\hbar^2}{2m_\ell} (k_x^2 + k_y^2 + k^2) + V_\ell[\{\bar{n}_i\} \; ; \; -\infty] \tag{34}$$

Using Eq. (24) in Eq. (34) we obtain

$$\varepsilon_\ell^\alpha = \frac{\hbar^2}{2m_\ell} (k_x^2 + k_y^2 + k^2) + \xi_\ell \phi(-\infty) + \frac{\delta E_{xc}[\{\bar{n}_i\}]}{\delta \bar{n}_\ell} \tag{35}$$

Substituting Eq. (27) in Eq. (35), we find

$$\varepsilon_\ell^\alpha = \frac{\hbar^2}{2m_\ell} (k_x^2 + k_y^2 + k^2) + \xi_\ell \phi(-\infty) + \bar{\mu}_\ell^{xc}(\{\bar{n}_i\}) \tag{36}$$

where $\bar{\mu}_\ell^{xc}$ is the exchange-correlation contribution to the bulk chemical potential of ℓ^{th} component. Eq. (36) holds only when the wave function is given by Eq. (33). In general, $\psi_\ell^\alpha(\underline{r})$ has the form

$$\psi_\ell^\alpha(\underline{r}) = \psi_\ell(k,z)\ e^{i(k_x x + k_y y)} \quad . \tag{37}$$

Substituting Eqs. (36) and (37) in Eq. (23) and expressing length in excitonic Bohr radius, the energy in excitonic Rydberg (1 Rydberg = $\frac{m_r e^4}{2\hbar^2\kappa^2}$) we find,

$$\left(-\frac{m_r}{m_\ell}\frac{d^2}{dz^2} + V_\ell^{eff}[\{n_i\}\ ;\ z]\right)\psi_\ell(k,z) = \frac{m_r}{m_\ell}\left(k^2 - \bar{k}_{F\ell}^2\right)\psi_\ell(k,z) \tag{38}$$

where $\bar{k}_{F\ell}^3 = 3\pi^2\bar{n}_\ell/\nu_\ell$, and m_r is the reduced mass. For the effective potential of the ℓ^{th} component, V_ℓ^{eff}, we obtain the expression,

$$\begin{aligned} V_\ell^{eff}[\{n_i\}\ ;\ z] = 8\pi\ \xi_\ell \int_{-\infty}^{z} dz'\ (z - z')\ [n_e(z') - n_h(z')] \\ - \bar{\mu}_\ell(\{\bar{n}_i\}) + \mu_\ell^{xc}(\{n_\ell\}) \quad , \end{aligned} \tag{39}$$

where $n_e(z)$ and $n_h(z)$ are, respectively, the electron and hole densities, and $\bar{\mu}_\ell$ is the bulk chemical potential of ℓ^{th} component. The exchange-correlation potential, μ_ℓ^{xc}, is given by Eq. (27).

From the ground state energy calculations for a homogeneous EHL, we know that to a very good approximation the electrons and holes contribute equally to exchange-correlation energy[26,37]. Therefore, it is reasonable to divide exchange and correlation contribution in the bulk equally among electrons and holes. In that case, Eq. (39) simplifies to

$$\begin{aligned} V_\ell^{eff}[\{n_i\}\ :\ z] = 8\pi\ \xi_\ell \int_{-\infty}^{z} dz'\ (z - z')\ [n_e(z') - n_h(z')] - \bar{\mu}_\ell(\bar{n}_\ell) \\ + \mu_\ell^{xc}(n_\ell(z)) \end{aligned} \tag{40}$$

The exchange-correlation potential is given by

$$\mu_{\ell}^{xc}(n_{\ell}) = \frac{d}{dn_{\ell}} (n_{\ell}\varepsilon_{\ell}^{xc}(n_{\ell})) \tag{41}$$

where $\varepsilon_{\ell}^{xc}(n_{\ell})$ is the exchange-correlation energy per particle. Defining a local value of r_s by

$$n_{\ell}(z) = 3/4\pi\, r_{s,\ell}^{3}(z) \tag{42}$$

the expression for $\varepsilon_{\ell}^{xc}(n_{\ell})$ that we have used, reads

$$\varepsilon_{\ell}^{xc}(n_{\ell}) = \begin{cases} \dfrac{\alpha}{r_{s,\ell}(z)} - \sum_{i=1}^{7} c(i)\, r_{s,\ell}^{b(i)-2}, & r_{s,\ell}(z) < r_o \\ \dfrac{\alpha}{r_{s,\ell}(z)} + \dfrac{0.5*B_o}{C_o + r_{s,\ell}(z)}, & r_{s,\ell}(z) > r_o \end{cases} \tag{43}$$

In Eq. (43) α is related to the coefficient of exchange energy, the c(i) are the coefficients of polynomial fit to correlation energy, and B_o and C_o are the coefficients of Wigner fit to correlation energy. The coefficients of polynomial and Wigner fits to correlation energy are obtained from fully self-consistent calculation of Vashishta et al.[26]. Their calculation includes the effects of anisotropy of conduction bands as well as multiple scattering of e - e, e - h and h - h. The binding energy, equilibrium density, the crical temperature, obtained by Vashishta et al., agree very well with experimental results. Values of α, c(i), B_o and C_o are given in Tables III and IV.

Performing the sum over bands and the lowest states in Eq. (25) [see Appendix I] we obtain,

$$n_{\ell}(Z) = \frac{\nu_{\ell}}{\pi^2} \int_{0}^{\bar{k}_{F\ell}} dk(\bar{k}_{F\ell}^{2} - k^2)\, [\psi_{\ell}(k,Z)]^2 \quad . \tag{44}$$

The EHL in Ge(4;2), Ge(1;2), Si(6;2) and Si(2;2) consists of three dis-

tinct components - electrons, light holes and heavy holes. Corresponding to each component we have a set of equations like Eqs. (38), (40) and (44). It is well known that density of states mass of light holes is much smaller than that of heavy holes with the consequence that the light hole contribution to equilibrium density is much smaller than that of heavy holes. Therefore, it is reasonable to solve only the set of equations for electrons and heavy holes. In the set of equations for holes we include the kinetic contribution of light holes by defining an effective hole mass, m_H^*:

$$m_H^* = m_{hh}[1 + (\frac{m_{\ell h}}{m_{hh}})^{3/2}]^{2/3} , \qquad (45)$$

where $m_{\ell h}$ and m_{hh} are, respectively, the light and heavy hole masses in Ge and Si. The use of m_H^* in Eq. (38), for example, insures an exact treatment of kinetic energy of holes in a homogeneous EHL. In Ge(1;1) and Si(2;1), there is only one hole band, with the consequence that there are only two sets of coupled equations to be solved.

We start with exponential trial density profiles for electrons and holes, and construct their effective potentials from Eq. (40). Having obtained the effective potentials, we solve Eq. (38) for $\psi_\ell(k,z)$ of each component and then use them in Eq. (44) to construct new densities $\{n_\ell(z)\}$. This procedure is continued until $\{n_\ell(z)\}$ converge satisfactorily. The degree of convergence that we attain for each density profile is better than 0.5% of the mean density. A further check on convergence is provided by the one-dimensional analog of Friedel sum rule[56] [see Appendix I] which is very well satisfied in our calculations [for details of our numerical procedure, see Appendix II].

The self-consistent density profiles in Ge(4; 2), Ge(1; 2), Ge(1; 1), Si(6; 2), Si(2; 2), and Si(2; 1) are shown in Figures (1) - (6). Tables V and VI contain

normalized values of $n_e(z)$ and $n_h(z)$ in the six systems. It is evident from Figures (1), (3), (4) and (6) that the hole density spills out more than the electron density in Ge(4; 2), Ge(1; 1), Si(6; 2), and Si(2; 1). The excess spilling of holes is due to the fact that in these four systems the binding energy of holes is less than that of electrons. It further indicates that in Ge(4; 2), Ge(1; 1), Si(6; 2) and Si(2; 1) one would expect the EHD to carry a negative charge. In Ge(1; 2) and Si(2; 2), there is an excess leakage of electrons than holes, indicating that the holes have a greater binding energy than electrons. Consequently, the EHD is expected to sustain a positive charge in Ge(1; 2) and Si(2; 2).

It is apparent from Figs. (1)-(6) that the larger the binding energy of a component, the bigger the amplitude of the first peak in Friedel oscillations. This trend is in line with the results of Lang and Kohn for a metal surface[55]. We would like to mention here that the Friedel oscillations in effective potential are not as pronounced as in electrostatic potential.

III. SURFACE ENERGY

The surface tension of EHL consists of three contributions; kinetic (σ_s), electrostatic (σ_{es}), and exchange and correlation (σ_{xc}).

$$\sigma = \sigma_s + \sigma_{es} + \sigma_{xc} \tag{46}$$

Each of these terms is further made up of contributions arising from electrons and holes. Using the superscript ℓ to denote a component of EHL, we shall give below the expressions for σ_s^ℓ, σ_{es}^ℓ and σ_{xc}^ℓ.

The expression for σ_s^ℓ is obtained in the same way Lang and Kohn did[55]. In terms of phase shifts and effective potential, kinetic contribution of ℓ^{th}

component to surface tension is

$$\sigma_s^{\ell}[n_\ell] = \frac{2\nu_\ell m_r}{\pi^2 m_\ell} \int_0^{\bar{k}_{F\ell}} dk\, k(\bar{k}_{F\ell}^2 - k^2)\{\frac{\pi}{4} - \gamma(k)\}$$

$$-\int_{-\infty}^{\infty} dz(V_\ell^{eff}[\{n_i\};z] - V_\ell^{eff}[\{\bar{n}_i\};-\infty)])n_\ell(z) \qquad (47)$$

In evaluating σ_s^{ℓ} it is extremely important that the Friedel sum rule[56] [see Appendix I] be well satisfied. Violation of Friedel sum rule can lead to serious errors in the kinetic contribution to surface energy.

The exchange and correlation contribution of ℓ^{th} component is given by

$$\sigma_{xc}^{\ell}[n_\ell] = \int_{-\infty}^{\infty} dz\, n_\ell(z)[\varepsilon_\ell^{xc}(n_\ell) - \varepsilon_\ell^{xc}(\bar{n}_\ell)] \,, \qquad (48)$$

where $\varepsilon_\ell^{xc}(n_\ell)$ is obtained from Eq. (43).

The electrostatic contribution to surface tension can be written as

$$\sigma_{es}[\{n_i\}] = \frac{1}{2}\int_{-\infty}^{\infty} dz\, \phi(z)[n_e(z) - n_h(z)]$$

where (49)

$$\phi(z) = 8\pi \int_z^{\infty} dz'(z-z')[n_e(z') - n_h(z')]$$

Using the self-consistent density profiles, effective potentials and phase shifts we evaluate the electrostatic, kinetic, and exchange-correlation contributions to surface tension. Table VII contains values of surface tenstion, σ, for EHL in Ge(4;2), Ge(1;2), Ge(1;1), Si(6;2), Si(2;2) and Si(2;1). We find that $\sigma = 3.7 \times 10^{-4}$ erg/cm^2 in Ge(4;2). It agrees favorably with the measurements of Westervelt et al.[39], Etienne et al.[41] and Staehli[42]. Note, the self-consistent value of σ in Ge(4;2) differs appreciably (almost a factor of 4) from the values obtained by Rice[37], Sander et al[46], and Reinecke and Ying[48]. It substantiates similar claims made by Lang and Kohn in the context

of a metal surface[55]. However, when one includes in the variational calculation the gradient correction to exchange and correlation energy[50,51], the value of σ in Ge(4;2) is found to be 3.5×10^{-4} erg/cm^2. Such an agreement between self-consistent and the variational calculations is rather fortuitous. Within the framework of density functional formalism, Rose and Shore have carried out a partial self-consistent calculation for EHL surface in Ge(4;2); the authors report a value of 2.6×10^{-4} erg/cm^2 for EHL surface tension[57]. We find that the value of σ in Ge(1;1) is a factor of twenty smaller than in Ge(4;2).

In Si(6;2), the surface tension of EHL is calculated to be 87.4×10^{-4} erg/cm^2 [58]. It is again a factor of three larger than the variational result of Reinecke and Ying[31]. The self-consistent result for σ in Si(2;1) is a factor of eight smaller than in Si(6;2). Considering the important role played by surface tension in the determination of coexistence curve, kinetics of EHD formation, and in establishing the validity of density functional formalism, there is a dire need for conclusive experiments on EHL surface in the various configurations of Ge and Si.

IV. CHARGE ON ELECTRON-HOLE DROP

Calculations for the ground state energy of a homogeneous EHL lead us to believe that the constituents of EHL, namely, electrons and holes, have different binding energies[20-26]. In the presence of a surface the difference in binding energies results in dissimilar density profiles for electrons and holes, and consequently in a dipole layer. The sign of dipole layer is dictated by the energetics of electrons and holes, since the purpose of dipole layer is to reduce the difference in their binding energies[37].

Following the conventional definition of dipole layer, we write

$$\Delta\phi = -8\pi \int_{-\infty}^{\infty} dz\ z[n_e(z) - n_h(z))]\ \text{Ry} \quad . \tag{50}$$

It is implicit in Eq. (50) that the total number of electrons is equal to the total number of holes. Using the self-consistent electron and hole densities, we calculate from Eq. (50) the values of dipole layer in the six configurations of Ge and Si. These values are given in Table VII. Evidently, holes have lesser binding energy than electrons in Ge(4;2) and Si(6;2). In order that the difference between the binding energies of holes and electrons be reduced by the presence of EHL surface the sign of dipole layer should be positive in Ge(4;2) and Si(6;2), which is indeed the case. Similar considerations lead us to conclude that $\Delta\phi$ should be negative in Ge(1;2) and Si(2;2) and positive in Ge(1;1) and Si(2;1).

Charge on EHD is determined by the difference in the chemical potentials of electrons and holes. In terms of bulk chemical potentials and dipole layer, this difference is given by (see Eq. (22)),

$$\mu_h - \mu_e = \bar{\mu}_h - \bar{\mu}_e - 2\Delta\phi \tag{51}$$

It is apparent from Table VII that the difference $\mu_h - \mu_e$ is positive in Ge(4:2) and Si(6;2), which means that the holes are less tightly bound than electrons. At a finite temperature ($T < T_c$, the transition temperature for EHL) there will be an excess thermionic emission of holes, and as a result the electron-hole droplet will acquire a negative charge whose magnitude will be determined by the condition that at equilibrium the work functions for electrons and holes become equal[52,58]. A similar situation occurs in Ge(1;1) and Si(2;1), wherein the EHD develops a negative charge. In Ge(1;2), however, we find that the difference $\mu_h - \mu_e$ is negative, implying that the EHD sustains a positive charge[52],

whereas in Si(2;2) we find that the difference $\mu_h - \mu_e$ is extremely small. Within the limits of accuracy of our calculations, we obtain a neutral EHD in Si(2;2). Insofar as the sign of charge is concerned, our results in Ge(4;2) and Ge(1;2) agree with the experiment of Pokrovsky and Svistunova[38]. Recent measurements of Nakamura has also shown that EHD is negative in Ge(4;2)[59]. No measurement of charge has yet been reported in Ge(1;1) or any of the configurations in Si.

There are two idealized situations in which one can determine the magnitude of charge on EHD. First, under pulsed excitation, i.e., when the medium outside of EHD is regarded as vacuum, the magnitude of charge, Q, is calculated from the equation[37]

$$Q = \frac{1}{2}\left[\sqrt{2 + R|\mu_h - \mu_e|} - 1\right]^2 \qquad (52)$$

where all the quantities are measured in reduced units. For a typical drop of radius $R = 284\ a_x (\sim 5 \times 10^{-4}\text{cm})$, we find that the EHD carries a charge of $-27|e|$ in Ge(4;2)[52]. Variational calculations of Rice[37], and Reinecke and Ying[48] yield $-18|e|$ and $+6|e|$, respectively. Calculation of Rose and Shore also yields a negative charge on EHD in Ge(4;2)[57]. The authors, however, do not quote the magnitude of charge.

The second situation occurs when the EHD becomes surrounded by ionized carriers. The problem is now much more complicated because of screening by free carriers. Assuming that the screening length is much less than the radius of EHD and treating ionized carriers as a classical gas, Rice obtains the following expression for the droplet charge[37]:

$$Q = \sqrt{2}\, r_D^{-1}\, k_B T\, R^2 \sinh\left(\frac{|\mu_h - \mu_e|}{2k_B T}\right), \qquad (53)$$

where Debye-Hückel screening length is given by

$$r_D = \left(\frac{k_B T}{8\pi n_i}\right)^{\frac{1}{2}} . \qquad (54)$$

All the quantities in Eqs. (53) and (54) are measured in reduced units. Under conditions of thermodynamic equilibrium at 4.2°K, the density of free carriers, $n_i = 2 \times 10^{-12} cm^{-3}$. Using this value of n_i we obtain a droplet charge of - 700|e| in Ge(4;2)[52]. Measurement of Pokrovsky and Svistunova yields a value of - 100|e|[38], while Nakamura obtains a value of -400|e| at 1.6°K.[59] The apparent discrepancy between theory and experiment is mainly due to the fact that theoretical estimates of charge[37,52] are made under the simplifying assumption that the screening length is much less than the radius of the drop. Also, the real experimental condition may not conform well to the above mentioned assumption. It should also be borne in mind that in the experimental determination of charge, there are ambiguities arising from the assumption of collision time[59].

It is evident from Eqs. (52) and (53) that in order to obtain the magnitude of charge one needs to know the radius of EHD. Experimental measurements of droplet radius have not yet been made in Ge(1;2), Ge(1;1), Si(2;2) and Si(2;1), which prevents us from estimating the charge on EHD in these systems.

CONCLUSION

We have shown that in order to resolve the question of EHD charge it is important to treat the kinetic energy of electrons and holes properly. Since the variational method provides a poor approximation for kinetic energy[37,48,50], it fails to account for the experimental observation that the EHD sustains a negative charge in Ge(4;2) and a positive charge in Ge(1;2)[38]. By solving a set of coupled Kohn-Sham equations for the constituents of EHD, we indeed find that the EHD is negatively charged in Ge(4;2) and positive in Ge(1;2). Although the Kohn-Sham procedure involves much more numerical work than the variational method, the former has the advantage that it treats kinetic energy exactly and also includes the effect of Friedel oscillations. On the basis of self-consistent calculation we predict that the EHD carries a negative charge in Ge(1;1).

Similar features are also expected to occur in silicon under a uniform stress along <100> direction. In Si(6;2) and Si(2;1) our calculations show that the EHD sustains a negative charge. However, in Si(2;2) we find that the electron-hole drop is almost neutral.

As regards surface tension of EHD, the value in Ge(4;2) agrees favorably with the experimental estimates of Westervelt et al.[39], Etienne et al.,[41] and of Staehli[42]. The self-consistent estimate of σ in Ge(1;1) is found to be a factor of twenty smaller than in Ge(4;2). The surface tension in Si(6;2) is calculated to be 87.4×10^{-4} erg/cm^2, a factor of eight larger than in Si(2;1). The values of σ in Ge(1;2) and Si(2;2) are found to be 1.0×10^{-4} and 32.8×10^{-4} erg/cm^2, respectively.

One of the approximations in this work amounts to dividing equally between electrons and holes the exchange and correlation energy per e - h pair in the bulk of electron-hole liquid. This is a reasonable approximation, since we

know from the ground state energy calculations for a uniform EHL that the electrons and holes contribute almost equally to the exchange-correlation energy[26,37]. One would expect it to be the case, because exchange and correlation effects arise from Pauli principle and Coulomb interaction. To avoid confusion, we would like to emphasize that this approximation does not imply that the exchange and correlation potentials for electrons and holes are equal in the surface region of EHL.

The major approximation in our calculation is that we have retained only the local density contribution to exchange-correlation potentials of electrons and holes. It may seem feasible to improve the local density approximation by including the exchange-correlation gradient corrections. The first gradient correction to exchange-correlation energy is typically of the form $\int d\underline{r}\ |\nabla n(\underline{r})|^2/n^{4/3}(\underline{r})$. It can be easily seen that the potential, obtained by taking the derivative with respect to $n(\underline{r})$, behaves pathologically in the tail region of density. For this reason, it is not possible to include in the self-consistent calculation the first gradient correction to exchange-correlation potential. One should note, however, that such a difficulty does not occur in variational calculations that include the first gradient correction to exchange-correlation energy, which is well behaved everywhere. Kohn and Sham have suggested including in the LDA not only the first gradient correction, but also the higher terms in the gradient expansion[44]. Such a calculation will involve enormous numerical work. Many calculations have demonstrated the appropriateness of local density approximation (LDA). Gunnarson et al. have used LDA in calculating the binding energy of hydrogen atom[60]. Their result for the binding energy differs from the exact value by less than two per cent. Tong and Sham have shown that the density of atoms, obtained in the local density approximation, agrees well with the Hartree-Fock calculations[53]. The classic work of Lang and Kohn also shows that the

LDA is a good approximation in the study of metal surfaces[55]. Recently, Ando has used it in the calculation of intersubband separation in Si inversion Layer[61]. His results are in excellent agreement with experiment.

In view of the fact that the EHD surface is a genuine inhomogeneous plasma of electrons and holes, it is an ideal system for testing the validity of density functional formalism; in particular, of local density approximation in the Kohn-Sham procedure. Thus there is a dire need of doing careful measurements of surface tension and charge on EHD in the aforementioned systems.

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APPENDIX I

Let us assume that the EHL has dimensions (L_x, L_y, $2L_z$) along the x,y and z directions. Further, we suppose that L_x, L_y >> $2L_z$ and that the geometrical surface of EHL lies at z = 0.

The Schrödinger-like equation for the ℓ^{th} component is given by

$$\{-\frac{\hbar^2}{2m_\ell}\frac{\partial^2}{\partial z^2} + V_\ell[\{n_i\}\ ;\ z]\}\ \psi_\ell(k,z) = \frac{\hbar^2 k^2}{2m_\ell}\ \psi_\ell(k,z) \qquad \text{(A-1)}$$

For the present discussion it is not necessary to specify the form of potential V_ℓ.

Multiplying Eq. (A-1) with $\psi_\ell(k',z)$, interchanging prime and unprimed quantities in the last equation and then subtracting the resulting equation we obtain,

$$\frac{\partial}{\partial z}\left[\psi_\ell(k',z)\frac{\partial\psi_\ell(k,z)}{\partial z} - \psi_\ell(k,z)\frac{\partial\psi_\ell(k',z)}{\partial z}\right] = (k'^2 - k^2)\psi_\ell(k',z)\psi_\ell(k,z) \qquad \text{(A-2)}$$

Integrating Eq. (A-2) from z to ∞ and taking the limit $k' \to k$, we find

$$\int_z^\infty dz'\ [\psi_\ell(k,z')]^2 = -\frac{1}{2k}\left[\frac{\partial\psi_\ell(k,z)}{\partial z}\frac{\partial\psi_\ell(k,z)}{\partial k} - \psi_\ell(k,z)\frac{\partial^2\psi_\ell(k,z)}{\partial z\partial k}\right] \qquad \text{(A-3)}$$

Deep inside the liquid, the wave function takes the form,

$$\left.\begin{aligned} &\psi_\ell(k,z) = A_\ell(k)\ \sin(kz - \gamma(k)) \\ &\text{where} \\ &k = \frac{m\pi}{2L_z} - \frac{\gamma(k)}{L_z}\ ,\ m = \text{even integer} \\ &\qquad\qquad \text{and } 0 \le \gamma(k) \le \pi/2 \end{aligned}\right\} \qquad \text{(A-4)}$$

Taking the limit $z = -L_z$ in Eq. (A-3) and making use of Eq. (A-4) we get

$$\int_{-L_z}^\infty dz'\ [\psi_\ell(k,z')]^2 = -\frac{\{A_\ell(k)\}^2}{2k}\left[-k(L_z + \gamma'(k)) + \frac{1}{2}\sin 2(kL_z + \gamma(k))\right] \qquad \text{(A-5)}$$

where $\gamma'(k) \equiv d\gamma(k)/dk$.

Making use of the fact that the wave function is either symmetric or anti-symmetric about $z = -L_z$, i.e.,

$$\int_{-\infty}^{-L_z} dz\ [\psi_\ell(k,z)]^2 = \int_{-L_z}^{\infty} dz\ [\psi_\ell(k,z)]^2 = \frac{1}{2L_xL_y} \quad , \tag{A-6}$$

we obtain from Eq. (A-5) the expression for the normalization constant $A_\ell(k)$:

$$\{ A_\ell(k)\}^2\ [1 + \frac{\gamma'(k)}{L_z}] = \frac{2}{\Omega_d} \quad , \tag{A-7}$$

where $\Omega_d = 2L_xL_yL_z$ is the volume of the electron-hole liquid.

The expression for the density of ℓ^{th} component [Eq. (25)] reads

$$n_\ell(\underline{z}) = 2\nu_\ell \sum_m \sum_{m_x} \sum_{m_y} |\psi_\ell(\underline{k},\underline{z})|^2 \quad , \tag{A-8}$$

where the factor of two arises from spin summation and ν_ℓ comes from the sum over the bands accommodating the particles of ℓ^{th} component. *The lowest filled states* are characterized by m, m_x and m_y, such that

$$(k_x,\ k_y,\ k) \equiv (\frac{2\pi m_x}{L_x} \ , \ \frac{2\pi m_y}{L_y} \ , \ \frac{m\pi}{2L_z} - \frac{\gamma(k)}{L_z}) \tag{A-9}$$

Now, the states in wave number space lie on sheets normal to k- axis and are spread according to Eq. (A-9). Since L_x, $L_y >> 2L_z$, the states on any sheet are much more densely packed than the spacing between the sheets. It is clear from Eq. (A-9) that on a given sheet there are $(L_xL_y/4\pi^2)$ states per unit area. We take the occupied states to lie within a hemisphere of radius $k_{\ell p}$ in the $k > 0$ half space. The hemisphere cuts the k- axis between R^{th} and $(R + 1)^{th}$ sheets such that

$$k_R \leq k_{\ell p} \leq k_{R+1} \tag{A-10}$$

The radius of the circular sheet, which accommodates particles of m^{th} state, is given by

$$[k_{\ell p}^2 - (\frac{m\pi}{2L_z} - \frac{\gamma(k)}{L_z})^2]^{\frac{1}{2}} \quad . \tag{A-11}$$

Therefore, the expression for $n_\ell(\underline{z})$ becomes,

$$n_\ell(z) = \nu_\ell (\frac{L_x L_y}{2\pi}) \sum_m |A_\ell(k)|^2 |\psi_\ell(k,z)|^2 (k_{\ell p}^2 - k^2) \tag{A-12}$$

Changing the sum over m in Eq. (A-12) into an integration over k and using Eq. (A-7) we obtain

$$n_\ell(z) = \frac{\nu_\ell}{\pi^2} \int_0^{k_{\ell p}} dk \; (k_{\ell p}^2 - k^2) |\psi_\ell(k,z)|^2 \tag{A-13}$$

where

$$\psi_\ell(k,z)_{z \to \pm L_z} \sin(kz - \gamma(k)) \tag{A-14}$$

Now, total number of particles of ℓ^{th} component is given by

$$N_\ell = 2\nu_\ell \sum_m \sum_{m_x} \sum_{m_y} 1 \tag{A-15}$$

Carrying out the summations in Eq. (A-15) we find

$$N_\ell = \Omega_d \, (\frac{\nu_\ell k_{\ell p}^3}{3\pi^2}) \, [1 - \frac{3}{k_{\ell p}^3 L_z} \int_0^{\bar{k}_{\ell p}} dk \; k\{\frac{\pi}{4} - \gamma(k)\}] \tag{A-16}$$

However,

$$\frac{N_\ell}{\Omega_d} = \frac{\nu_\ell \bar{k}_{F\ell}^3}{3\pi^2} \quad . \tag{A-17}$$

Comparing Eqs. (A-16) and (A-17), we obtain

$$k_{\ell p} = \bar{k}_{F\ell} [1 + \frac{1}{\bar{k}_{F\ell}^3 L_z} \int_0^{\bar{k}_{F\ell}} dk \; k\{\frac{\pi}{4} - \gamma(k)\}] + O(\frac{1}{L_z^2}) \tag{A-18}$$

In the limit $z \to - L_z$, we obtain from Eq. (A-13)

$$n_\ell(-L_z) = \frac{\nu_\ell k_{\ell p}^3}{3\pi^2} + O(\frac{1}{L_z^2}) \qquad \text{(A-19)}$$

Owing to the fact that no free charges can exist deep inside the EHL, we demand

$$n_\ell(z)\big|_{z=-L_z} = \frac{N_\ell}{\Omega_d} = \frac{\nu_\ell \bar{k}_{F\ell}^3}{3\pi^2} \qquad \text{(A-20)}$$

and therefore from the last two equations we find

$$k_{\ell p} = \bar{k}_{F\ell} + O(1/L_z^2) \qquad \text{(A-21)}$$

In order that Eq. (A-21) be consistent with Eq. (A-18), we must demand that for each component ℓ,

$$\int_0^{\bar{k}_{F\ell}} dk\ k\gamma(k) = \frac{\pi}{8}\bar{k}_{F\ell}^2 \qquad \text{(A-22)}$$

and thus

$$n_\ell(z) = \frac{\nu_\ell}{\pi^2}\int_0^{\bar{k}_{F\ell}} dk\ (\bar{k}_{F\ell}^2 - k^2)\ |\psi_\ell(k,z)|^2 \qquad \text{(A-23)}$$

Equation (A-22) is the one-dimensional analog of Friedel sum rule[56]. It provides a check on the phase shift obtained from the wave functions. Further, by satisfying this sum rule one insures that both the electron and hole densities are equal to the mean density deep inside the liquid.

APPENDIX II

We shall deal here with the numerical procedure used in solving a set of coupled Kohn-Sham equations for the case of EHL surface. Our procedure is a generalization of that developed by Lang and Kohn for a metal surface[55].

We start with trial density profiles for electrons and holes. These profiles decay exponentially outside the surface and approach the mean bulk density well inside the surface. Further, the parameters in the initial profiles are so chosen that we obtain overall charge neutrality:

$$\int_{-\infty}^{\infty} dz\, n_e(z) = \int_{-\infty}^{\infty} dz\, n_h(z) \qquad \text{(B-1)}$$

Using the trial profiles in Eq. (40) we calculate the effective potentials for electrons and holes. Substituting the effective potential in Eq. (38), we solve it for $\psi_\ell(k,z)$ in the range 0 to $\bar{k}_{F\ell}$. Imposing the condition that the wavefunction should approach a sine wave deep inside the electron-hole liquid, i.e.,

$$\psi_\ell(k,z) \underset{z \to -\infty}{\sim} A_\ell(k)\, \sin(kz - \gamma(k)) \qquad \text{(B-2)}$$

we obtain $\gamma(k)$ from Eq. (B-2) and check if the phase shifts satisfy the phase rule[56] [Eq. (A-22)],

$$\int_0^{\bar{k}_{F\ell}} dk\, k\gamma(k) = \frac{\pi}{8}\, \bar{k}_{F\ell}^2 \qquad \text{(B-3)}$$

for every component. If the phase rule is not satisfied to a few percent, we discard the initial trial profiles, choose a new set of parameters in the initial profiles and follow the aforementioned procedure until Eq. (B-3) is almost satisfied. Note, imposition of phase rule is another way of insuring that the densities approach the correct bulk values deep inside the EHL. The asymptotic form for wavefunctions [Eq. (B-2)] is ideally achieved only if $z \to -\infty$. How-

ever, in practice it is not feasible to go to an arbitrarily long distance inside the liquid. Therefore, one has to introduce correction terms to Eq. (B-2). In order to deal effectively with the asymptotic region we observe that the density of ℓ^{th} component assumes the following asymptotic form:

$$n_\ell(z)_{z \to -\infty} \bar{n}_\ell[1 + \frac{3 \cos 2(\bar{k}_{F\ell} z - \gamma(\bar{k}_{F\ell}))}{(2\bar{k}_{F\ell} z)^2}] + O(\frac{1}{z^3}) \qquad \text{(B-4)}$$

With this form for the densities, the asymptotic value of potential of ℓ^{th} component becomes

$$V_\ell^{eff}[\{n_\ell\}\ ;\ z]_{z \to -\infty} - \frac{m_r}{m_\ell} \bar{k}_{F\ell}^2 + \sum_{\ell'} P_{\ell,\ell'} \cos 2(\bar{k}_{F\ell'} z - \gamma(\bar{k}_{F\ell'}))/z^2 + O(1/z^3) \qquad \text{(B-5)}$$

The coefficients $P_{\ell,\ell'}$ are determined by fitting the effective potentials to Eq. (B-5). Using this asymptotic form for effective potential we find $1/z^2$ correction term to the asymptotic value of wavefunction $\psi_\ell(k,z)$, namely, Eq. (B-2). Now the wavefunction is fitted to a form given in Eq. (B-2) plus the $1/z^2$ correction term. From such a fit we extract the value of normalization constant $A_\ell(k)$.

The expression for density involves $\psi_\ell(k,z)$, which must attain a sinusoidal form deep inside the liquid. In order that the density of a given component attains its correct bulk value, the amplitude of the sine wave must be unity. Thus, the knowledge of $A_\ell(k)$ enables one to construct $\psi_\ell(k,z)$ such that

$$\psi_\ell(k,z)_{z \to -\infty} \sin(kz - \gamma(k)) \qquad \text{(B-6)}$$

We substitute these $\psi_\ell(k,z)$ in Eq. (44) to obtain the density $n_\ell(z)$. When the new $\{n_\ell(z)\}$ are close to the initial density profiles, we resort to a linear response procedure to bring about self-consistency. Let us denote by $\{n_\ell^0\}$

and $\{n_\ell^{(1)}\}$ the trial densities and the densities obtained after first iteration. Then, the set of Eqs. (38), (40), and (44) [with $\{n_\ell\}$ replaced by $\{n_\ell^0\}$ in Eqs. (38) and (40) and $\{n_\ell^{(1)}\}$ in Eq. (44)] may be taken to define the following functional relationship:

$$\{n_\ell^{(1)}\} = F[\{n_\ell^0\} \; ; \; z] \tag{B-7}$$

Using the set of densities $\{n_\ell^{(1)}\}$, we obtain from Eqs. (38), (40), and (44) another set of densities $\{n_\ell^{(2)}\}$.

In the spirit of Eq. (B-7) we write

$$\{n_\ell^{(2)}\} = F[\{n_\ell^{(1)}\} \; ; \; z] \tag{B-8}$$

In order that $\{\tilde{n}_\ell\}$ be the true solutions we must have

$$\{\tilde{n}_\ell\} = F[\{\tilde{n}_\ell\} \; ; \; z] \tag{B-9}$$

Let us assume that the addition of $\{\delta n_\ell^{(1)}\}$ to $\{n_\ell^{(1)}\}$ brings about self-consistency. Then we obtain from Eq. (B-9):

$$n_\ell^{(1)} + \delta n_\ell^{(1)} = F_\ell[\{n_\ell^{(1)} + \delta n_\ell^{(1)}\} \; ; \; z] \tag{B-10}$$

Since $\{n_\ell^{(1)}\}$ are close to the true solutions, the quantities $\{\delta n_\ell^{(1)}\}$ must be small compared to $\{n_\ell^{(1)}\}$. Making a Taylor series expansion of the r.h.s. of Eq. (B-10), we find

$$n_\ell^{(1)} + \delta n_\ell^{(1)} = n_\ell^{(2)} + \sum_{i=1}^{M} \int_{-\infty}^{\infty} \delta n_i^{(1)}(z') \frac{\delta F_\ell[\{n_i^{(1)}\} \; ; \; z]}{\delta n_i^{(1)}(z')} \, dz' \tag{B-11}$$

We choose for $\delta n_\ell^{(1)}$ a linear combination of derivatives of harmonic oscillator functions:

$$\delta n_\ell^{(1)} = - \sum_{i=1}^{NH} a_\ell(i) \, Q_i(z) \quad , \tag{B-12}$$

where $Q_i(z)$ are derivatives of harmonic oscillator functions, NH the number of such functions, and $a_\ell(i)$ are the coefficients whose determination shall

enable us to obtain the self-consistent density profiles. In order that $\{Q_i(z)\}$ form a basis set, NH must be infinite. However, in practice, one needs a reasonably large but finite number (~20) of $Q_i(z)$ to achieve convergence. Substituting Eq. (B-12) in (B-11) and using the definition of a functional derivative, we obtain

$$n_\ell^{(1)} - n_\ell^{(2)} = \sum_{i=1}^{M} \sum_{j=1}^{NH} \frac{a_i(j)}{\lambda} \left(F[n_1, n_i - \lambda Q_j, --] - F[n_1, n_i, --] + \lambda \delta_{i\ell} Q_j\right) \qquad \text{(B-13)}$$

where λ is a small parameter. Multiplying Eq. (B-13) with harmonic oscillator functions, $P_j,(z)$, and integrating over z we obtain

$$\int_{-\infty}^{\infty} dz\,[n_\ell^{(1)}(z) - n_\ell^{(2)}(z)]P_j,(z) = \sum_{i=1}^{M} \sum_{j=1}^{NH} \frac{a_i(j)}{\lambda} \int_{-\infty}^{\infty} dz\; P_j,(z)\left(F_\ell[n_1, n_i - \lambda Q_j, --]\right.$$

$$\left. - F[n_1, n_i, --] + \lambda \delta_{i\ell} Q_j\right) \qquad \text{(B-14)}$$

To make this procedure effective one has to choose carefully the position and width of harmonic oscillator functions. It is our experience that these functions should always be centered near the surface and their width should be on the order of surface thickness.

From equations such as (B-14) we obtain the coefficients $a_i(j)$ and subsequently use them in Eq. (B-12) to obtain $\delta n_\ell^{(1)}$. Straightforward addition of $\delta n_\ell^{(1)}$ to $n_\ell^{(1)}$ yields the self-consistent values of density of ℓ^{th} component.

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Table 1 - List of band masses, dielectric constant and the value of excitonic rydberg in Ge (4;2) and Si (6;2). m_{el} and m_{et} are, respectively, the longitudinal and transverse masses for an electron, m_{oe} and m_{de} the optical and density of states masses for an electron, and $m_{\ell h}$ and m_{hh} are the light and heavy hole masses. These masses are given in units of bare electron mass. κ is the dielectric constant of the system and E_x is the value of excitonic rydberg. The values of band masses, κ and E_x in Ge (1;2) and Si (2;2) are the same as in Ge (4;2) and Si (6;2), respectively.

SYSTEM	m_{el}	m_{et}	m_{oe}	m_{de}	$m_{\ell h}$	m_{hh}	κ	E_x(meV)
Ge (4;2)	1.58	0.082	0.120	0.22	0.042	0.347	15.36	2.65
Si (6;2)	0.9163	0.1905	0.2588	0.32	0.154	0.523	11.4	12.85

Table II - Values of constants in Ge (1;1) and Si (2;1). The masses are measured in units of bare electron mass. m_{de} and m_{dh} are the density of states masses for an electron and hole; m_{oe} and m_{oh} are their optical masses. m_{hl} and m_{ht} are the longitudinal and transverse masses for a hole. E_x is the value of excitonic rydberg in Ge (1;1) and Si (2;1).

SYSTEM	m_{el}	m_{et}	m_{de}	m_{oe}	m_{hl}	m_{ht}	m_{dh}	m_{oh}	E_x(meV)
Ge(1;1)	1.580	0.082	0.2198	0.120	0.040	0.130	0.088	0.075	2.65
Si(2;1)	0.9163	0.1905	0.3216	0.2588	0.1988	0.2561	0.2354	0.2336	12.85

Table III - Coefficients of exchange and correlation energy per particle in unstressed Ge and Ge under uniform, uniaxial stress along <111> direction. The coefficient of exchange energy, α, is measured in excitonic rydberg. For $r_s(Z) < r_o$ correlation energy is fitted to a polynomial in $r_s(Z)$, where $r_s(Z) = \{\frac{4\pi}{3}n(Z)\}^{-1/3}$. Coefficients of the polynomial fit are given by $c(i) = 0.5 * A(i)/b(i)$ where $b(i) = i + 0.25$. Correlation energy is taken to be of the Wigner form for $r_s(Z) > r_o$. B_o and C_o are the coefficients of the Wigner fit. A(i) and B_o are expressed in excitonic rydberg; C_o and r_o are dimensionless.

COEFFICIENTS	Ge(4;2)	Ge(1;2)	Ge(1;1)
α	-0.5681	-0.7090	-0.8297
A(1)	0.7212729	0.4125300	0.4683857
A(2)	4.1265679	4.0192903	1.8475582
A(3)	-9.6488301	-9.4066370	-1.5382064
A(4)	13.9998052	13.2843140	0.9232383
A(5)	-10.3165219	-9.2912027	-0.2690568
A(6)	3.5668684	3.0446329	0.0282182
A(7)	-0.4567422	-0.3725362	0.0
B_o	-3.10247	-3.27550	-4.21484
C_o	1.45138	2.18922	3.91350
r_o	2	2	3

Table IV - Values of coefficients of exchange and correlation energy per particle in Si(6;2), Si(2;2), and Si(2;1). The coefficients of polynomial fit to correlation energy are given by c(i) = 0.5*A(i)/b(i), where b(i) = i + 0.25. Values of α, A(i), B_o, C_o, and r_o are tabulated below. Note, α, A(i), and B_o are measured in units of excitonic rydberg. C_o and r_o are dimensionless.

COEFFICIENTS	Si(6;2)	Si(2;2)	Si(2;1)
α	-0.5832	-0.6891	-0.8026
A(1)	0.7105611	0.4000295	0.4362952
A(2)	3.5159968	4.8634251	2.3587707
A(3)	-6.5141196	-13.0590236	-3.1982320
A(4)	8.0945300	20.4316281	3.4135213
A(5)	-5.4580137	-15.6070080	-1.9050812
A(6)	1.7901528	5.5015154	0.4931726
A(7)	-0.2217641	-0.7125849	-0.0469333
B_o	-3.32745	-3.16211	-4.21917
C_o	1.76294	1.95952	3.93928
r_o	2	2	3

Table V. Self-consistent density profiles of electrons and holes in Ge(4;2), Ge(1;2), and Ge(1;1). The origin, z = 0, is taken to be the position of geometrical surface of EHL. The distance, z, is measured in units of excitonic Bohr radius, a_x (≈177Å), and the densities in units of a_x^{-3}. In this table the densities have been normalized to the mean e-h pair density. Although we calculate the density profiles at points separated by a distance of 0.15 a_x, we quote the values of $n_e(z)$ and $n_h(z)$ only at every other point.

	Ge(4;2)		Ge(1;2)		Ge(1;1)	
z	$n_e(z)$	$n_h(z)$	$n_e(z)$	$n_h(z)$	$n_e(z)$	$n_h(z)$
-5.85	1.000	1.001	0.997	0.996	0.996	0.998
-5.55	1.007	1.004	0.997	0.996	0.985	0.991
-5.25	1.002	1.003	1.001	1.002	0.983	0.990
-4.95	1.001	1.000	1.005	1.006	0.994	0.995
-4.65	0.993	0.994	1.000	1.000	1.004	1.002
-4.35	1.002	1.003	0.995	0.994	1.017	1.009
-4.05	1.009	1.008	0.996	0.995	1.020	1.002
-3.75	1.005	0.999	1.005	1.007	1.015	1.008
-3.45	0.989	0.989	1.006	1.007	0.994	0.998
-3.15	0.985	0.991	0.997	0.996	0.976	0.985
-2.85	0.994	0.996	0.990	0.987	0.963	0.981
-2.55	1.015	1.011	0.999	0.999	0.974	0.986
-2.25	1.017	1.013	1.012	1.015	0.996	1.004
-1.95	0.989	0.990	1.006	1.008	1.033	1.019
-1.65	0.974	0.980	0.985	0.982	1.055	1.017
-1.35	0.997	1.001	0.981	0.976	1.043	0.988
-1.05	1.030	1.022	1.003	1.006	0.975	0.908

Table V (Cont'd)

	Ge(4;2)		Ge(1;2)		Ge(1;1)	
z	$n_e(z)$	$n_h(z)$	$n_e(z)$	$n_h(z)$	$n_e(z)$	$n_h(z)$
-0.75	1.010	0.992	0.979	0.999	0.852	0.797
-0.45	0.871	0.859	0.840	0.864	0.682	0.649
-0.15	0.602	0.610	0.594	0.606	0.507	0.500
0.15	0.315	0.336	0.344	0.336	0.344	0.366
0.45	0.135	0.139	0.166	0.150	0.208	0.248
0.75	0.046	0.049	0.069	0.053	0.122	0.166
1.05	0.014	0.017	0.026	0.017	0.066	0.106
1.35	0.002	0.003	0.008	0.004	0.027	0.059
1.65	0.000	0.001	0.002	0.001	0.011	0.031
1.95	0.000	0.000	0.001	0.000	0.006	0.019
2.25	0.000	0.000	0.000	0.000	0.003	0.014
2.55	0.000	0.000	0.000	0.000	0.001	0.010
2.85	0.000	0.000	0.000	0.000	0.000	0.007

Table VI Self-consistent electron and hole densities in Si(6;2), Si(2;2) and Si(2;1). z is measured in units of excitonic Bohr radius, a_x(≃50Å), and the densities in a_x^{-3}. The origin is taken to be the position of the geometrical surface of EHL. In this table the densities have been normalized to the mean e - h pair density.

z	Si(6;2)		Si(2;2)		Si(2;1)	
	$n_e(z)$	$n_h(z)$	$n_e(z)$	$n_h(z)$	$n_e(z)$	$n_h(z)$
-5.85	0.996	0.995	1.006	1.002	1.011	1.004
-5.55	0.992	0.994	1.000	0.996	1.017	1.003
-5.25	0.987	0.987	0.994	0.994	1.014	1.001
-4.95	0.994	0.997	0.992	0.997	1.010	1.000
-4.65	1.004	1.007	0.992	1.000	1.002	0.999
-4.35	1.012	1.011	1.000	1.004	0.990	0.998
-4.05	1.013	1.011	1.008	1.004	0.979	0.996
-3.75	1.016	1.011	1.013	1.003	0.974	0.993
-3.45	1.002	1.002	1.012	1.003	0.977	0.992
-3.15	0.990	0.995	1.001	1.001	0.986	0.994
-2.85	0.977	0.981	0.987	0.998	1.006	1.001
-2.55	0.981	0.982	0.978	0.991	1.031	1.008
-2.25	1.003	1.009	0.982	0.988	1.052	1.022
-1.95	1.030	1.032	1.002	0.993	1.058	1.022
-1.65	1.048	1.035	1.025	1.008	1.037	0.997
-1.35	1.034	1.013	1.029	1.017	0.982	0.953
-1.05	0.971	0.949	0.986	0.988	0.893	0.869
-0.75	0.852	0.841	0.880	0.901	0.772	0.757
-0.45	0.684	0.700	0.721	0.746	0.631	0.631
-0.15	0.496	0.523	0.536	0.553	0.487	0.499
0.15	0.332	0.339	0.357	0.367	0.356	0.370
0.45	0.197	0.204	0.218	0.211	0.244	0.268

Table VI (Cont.)

z	Si(6;2)		Si(2;2)		Si(2;1)	
	$n_e(z)$	$n_h(z)$	$n_e(z)$	$n_h(z)$	$n_e(z)$	$n_h(z)$
0.75	0.103	0.106	0.122	0.109	0.158	0.181
1.05	0.053	0.055	0.063	0.050	0.095	0.122
1.35	0.026	0.028	0.031	0.021	0.057	0.073
1.65	0.008	0.010	0.015	0.008	0.036	0.048
1.95	0.002	0.003	0.006	0.003	0.019	0.030
2.25	0.001	0.001	0.002	0.001	0.008	0.016
2.55	0.000	0.000	0.001	0.000	0.003	0.008
2.85	0.000	0.000	0.000	0.000	0.001	0.004

Table VII - Results from self-consistent calculation for the surface properties of EHD in Ge(4;2), Ge(1;2), Ge(1;1), Si(6;2), Si(2;2), and Si(2;1). σ is the surface tension of EHD. $\bar{\mu}_e$ and $\bar{\mu}_h$ are the bulk chemical potentials of electrons and holes. These are obtained from the fully self-consistent calculation of Vashishta et. al.[26] $\Delta\phi$ denotes the dipole layer.

SYSTEM	σ(erg/cm^2)	$\bar{\mu}_e$(meV)	$\bar{\mu}_h$(meV)	$\bar{\mu}_h-\bar{\mu}_e$	$2\Delta\phi$(meV)	SIGN OF CHARGE
Ge(4;2)	3.7×10^{-4}	-3.62	-2.21	1.41	0.77	NEGATIVE
Ge(1;2)	1.0×10^{-4}	-1.75	-2.76	-1.01	-0.98	POSITIVE
Ge(1;1)	0.2×10^{-4}	-2.17	-0.93	1.24	1.20	NEGATIVE
Si(6;2)	87.4×10^{-4}	-14.01	-7.84	6.17	3.34	NEGATIVE
Si(2;2)	32.8×10^{-4}	-8.87	-9.89	-1.02	-1.02	NEUTRAL*
Si(2;1)	11.4×10^{-4}	-9.77	-4.88	4.89	3.86	NEGATIVE

*In Si(2;2), we find that the difference in the chemical potentials of holes and electrons ($= \bar{\mu}_h - \bar{\mu}_e - 2\Delta\phi$) is a very small negative quantity, which implies that the drop is positively charged. However, considering the limit of accuracy of the calculation we can only conclude that the EHD is neutral in Si(2;2).

FIGURE CAPTIONS

Fig. 1:

Self-consistent density profiles of electrons and holes in Ge(4;2). Solid curve-electron density, $n_e(z)$; dashed curve-hole density, $n_h(z)$. The distance z is measured in units of excitonic Bohr radius, a_x(= 177 Å in Ge), and the densities are in units of a_x^{-3}. In Fig. (1), $n_e(z)$ and $n_h(z)$ are normalized to the mean particle density (= $3/4\pi r_s^3$ where r_s is the average interparticle separation) in homogeneous EHL. Note, the hole density spills out more than the electron density, because the binding energy of holes is less than that of electrons ($\bar{\mu}_h - \bar{\mu}_e$ = 1.41 meV). This is why the EHD sustains a negative charge in Ge(4;2).

Fig. 2:

Normalized self-consistent electron and hole densities as a function of z in Ge(1;2). Solid curve-electron density; dashed curve-hole density. In Ge(1;2), the binding energy of electrons is smaller than that of holes ($\bar{\mu}_h - \bar{\mu}_e$ = -1.01 meV), causing the electron density to spill out more than the hole density.

Fig. 3:

Normalized self-consistent electron and hole density profiles in Ge(1;1). Solid curve-electron density; dashed curve-hole density. Note, the hole density tail is longer than that of electrons. It is a consequence of the fact that the binding energy of electrons is larger than that of holes ($\bar{\mu}_h - \bar{\mu}_e$ = 1.24 meV).

Fig. 4:

Self-consistent electron and hole densities as a function of z in Si(6;2). Unit of distance is excitonic Bohr radius, a_x (= 49 Å in Si), and the unit of

density is a_x^{-3} . The electron and hole densities are normalized to the mean particle density in the homogeneous EHL. Since the binding energy of electrons is larger than that of holes ($\bar{\mu}_h - \bar{\mu}_e$ = 6.17 meV), the electron density spills out less than the hole density in Si(6;2).

Fig. 5:

Normalized self-consistent density profiles for electrons and holes in Si(2;2). Solid curve-electrons; dashed curve-holes. In Si(2;2), the binding energy of electrons is smaller than that of holes, which should lead to a positive charge on the drop. But the small difference in the chemical potentials of electrons and holes ($|\bar{\mu}_h - \bar{\mu}_e|$ = 1.02 meV, compared to 6.17 meV in Si(6;2) and 4.89 meV in Si(2;1), see Table VII) is almost compensated by twice the dipole layer. Thus, within the limits of accuracy of the calculation, our conclusion is that the drop is almost neutral.

Fig. 6:

Normalized self-consistent electron (solid curve) and hole (dashed curve) densities as a function of z in Si(2;1). It is evident from the smaller electron density tail that the electrons are more tightly bound than the holes, ($\bar{\mu}_h - \bar{\mu}_e$ = 4.89 meV), thereby giving rise to a negative charge on the EHD.

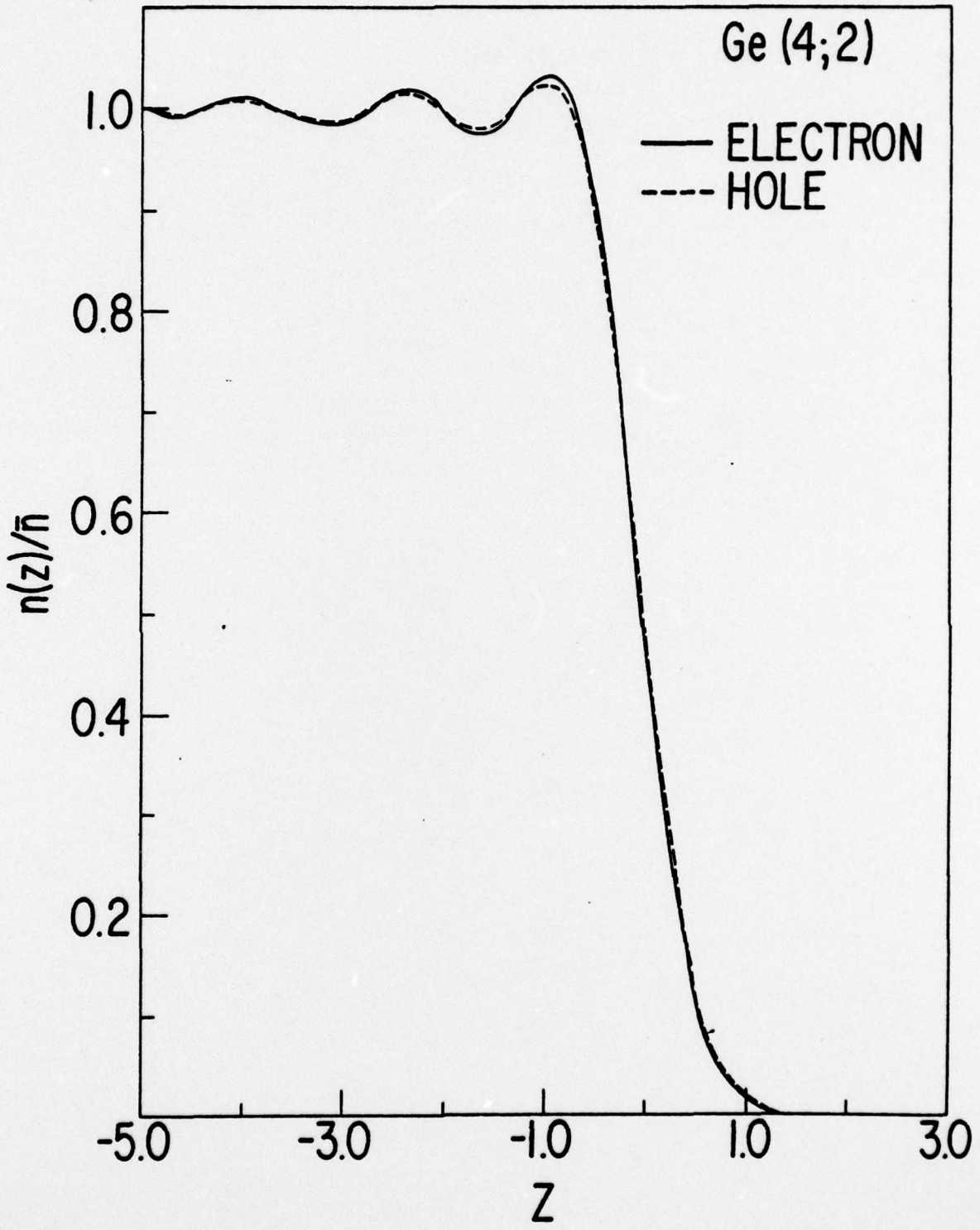

Figure 1

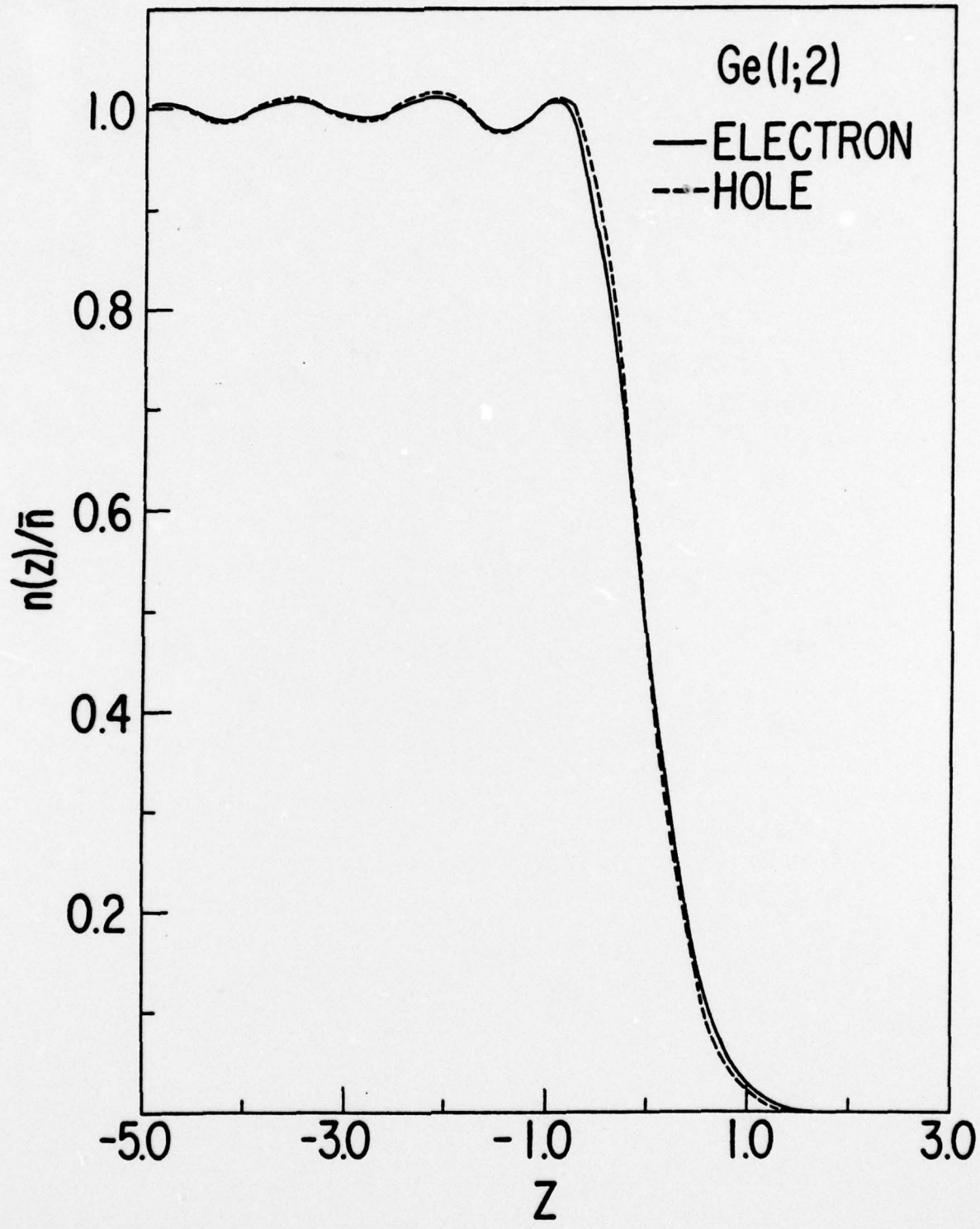

Figure 2

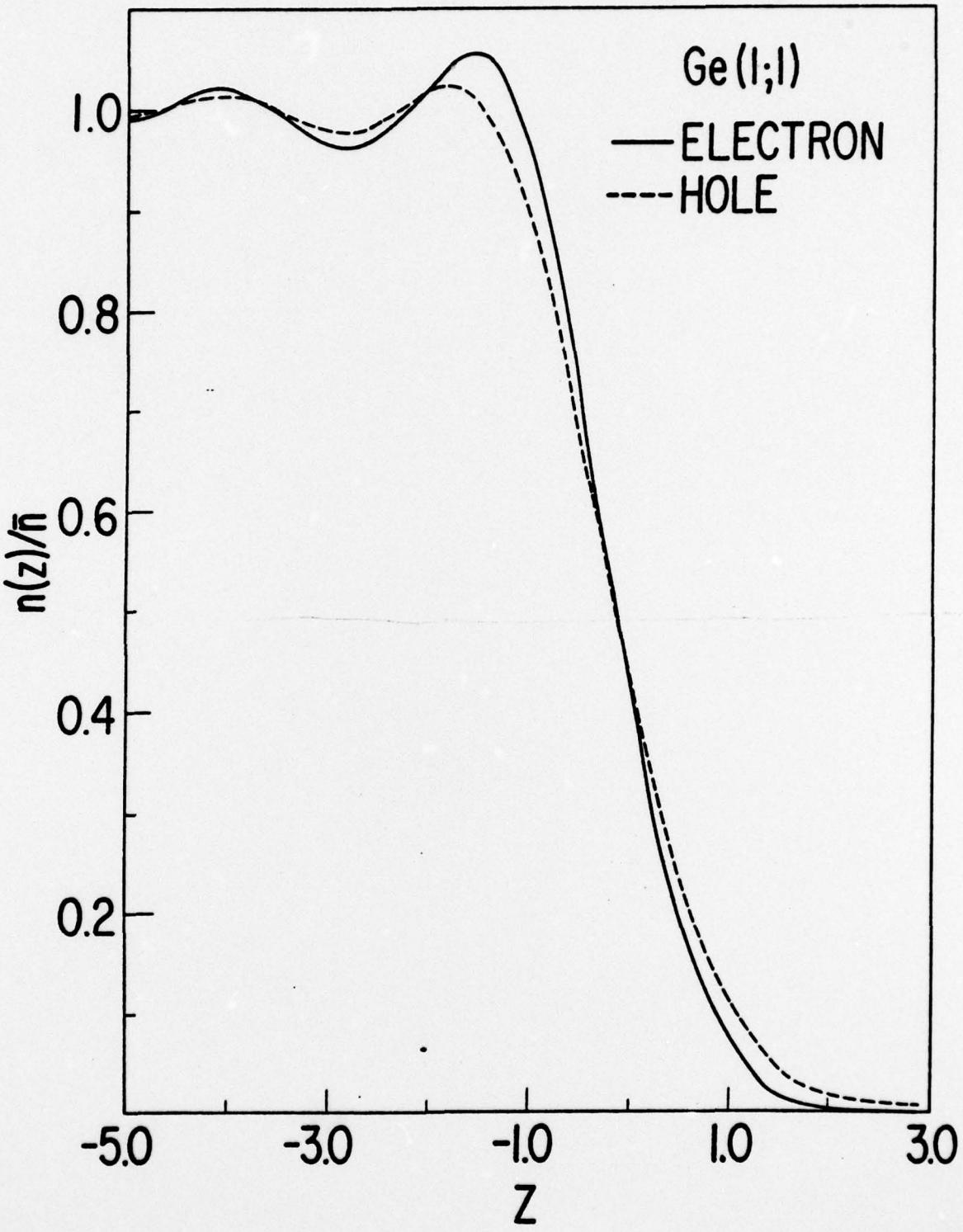

Figure 3

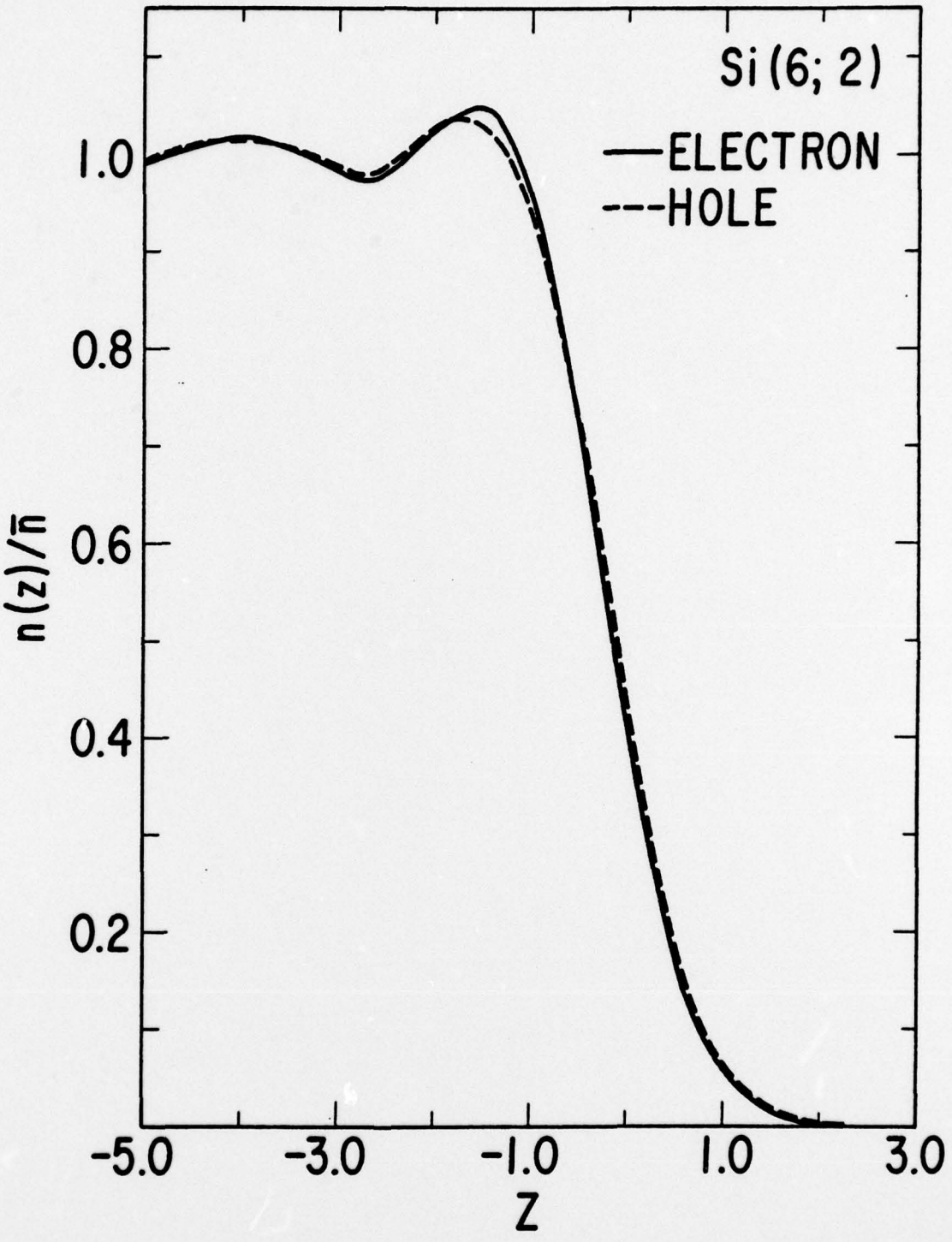

Figure 4

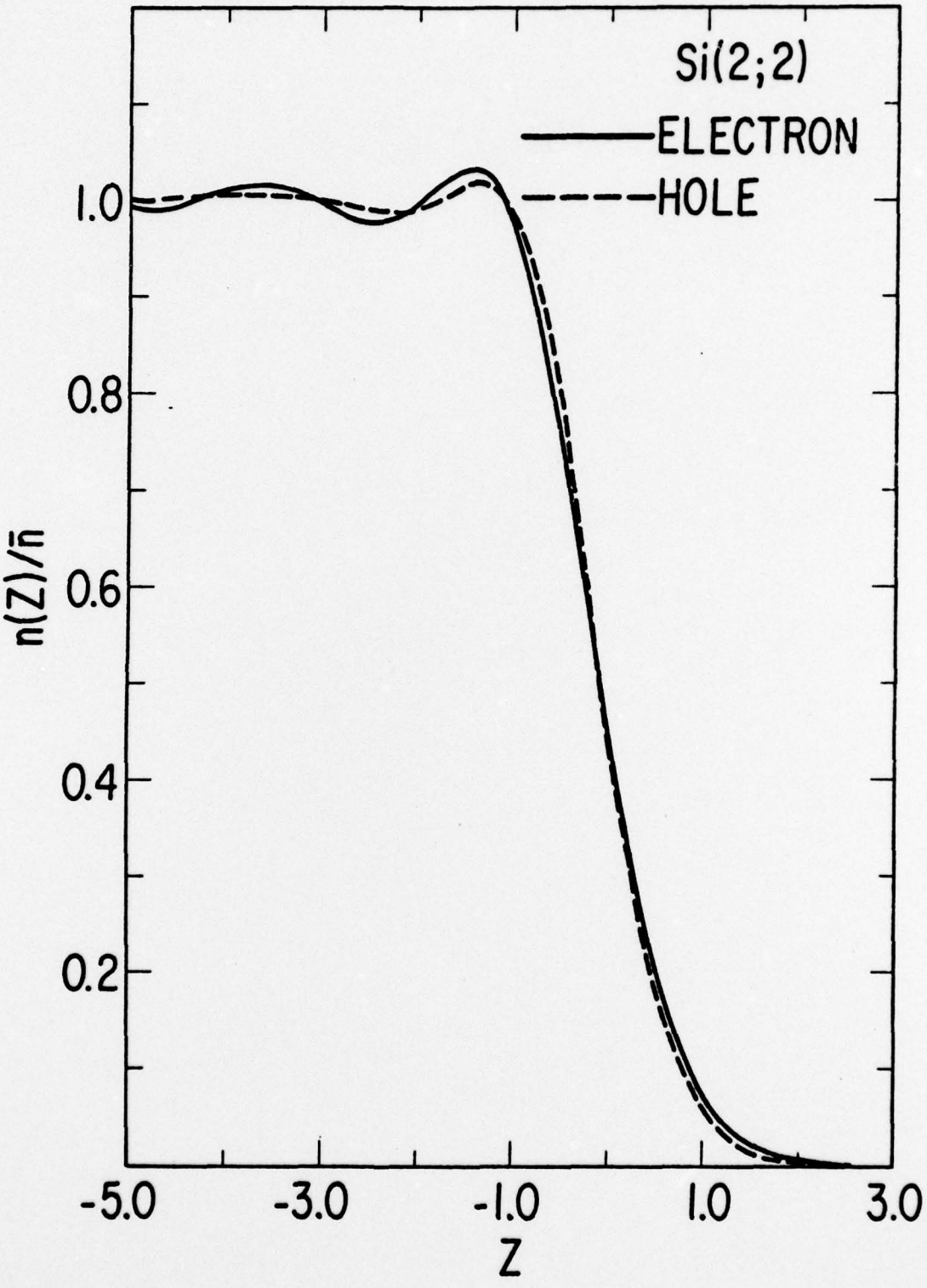

Figure 5

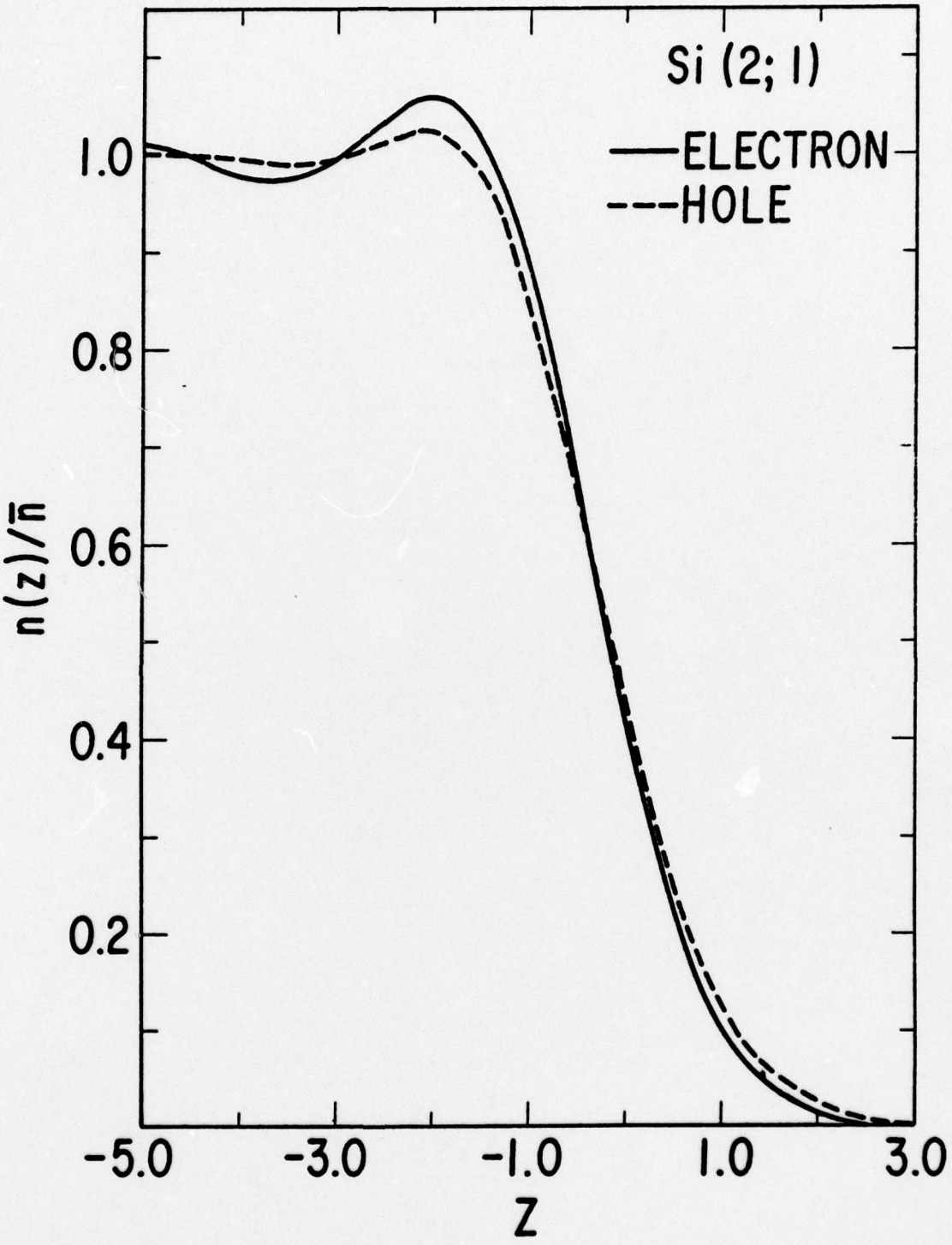

Figure 6